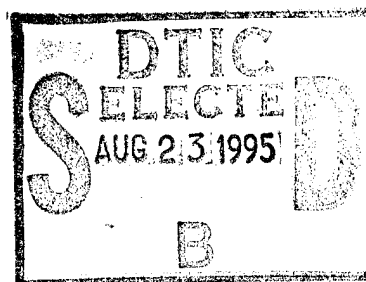Report No. 2.LC.APL.95

Synchronous Picosecond Sonoluminescence

Lawrence A. Crum

Applied Physics Laboratory
University of Washington
1013 NE 40th Street
Seattle, WA 98105

20 July 1995

Annual Summary Report

1 June 1994 - 31 May 1995

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The discovery of a single-bubble sonoluminescence has led to several interesting and remarkable observations. Among these are picosecond-length light flashes and a level of syncronicity several orders of magnitude greater than the period of the applied acoustic field. Although new and unique observations concerning this phenomenon are being rapidly reported, an adequate explanation for the physical mechanisms that give rise to single-bubble sonoluminescence has never been given. We describe here a few highlights of our recent research in our ongoing efforts to understand this complex phenomenon.

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Table of Contents

Project Title:

Synchronous Picosecond Sonoluminescence

Project Description:

The discovery of single-bubble sonoluminescence [Gaitan and Crum, 1990] has lead to several interesting and remarkable observations [Barber and Putterman, 1991]. Among these are picosecond-length light flashes and a level of synchronicity several orders of magnitude greater than the period of the applied acoustic field. Although new and unique observations concerning this phenomenon are being rapidly reported, an adequate explanation for the physical mechanisms that give rise to single-bubble sonoluminescence has never been given. We describe here a few highlights of our recent research in our ongoing efforts to understand this complex phenomenon.

Some Initial Results:

We report here on two specific aspects of our current research. More detail is contained in our recent publications.

A. Nonlinear Bjerknes Force.

If a gas bubble is positioned within an acoustic stationary wave, and driven at a frequency below it natural resonance frequency, it will experience radiation pressure forces, called Bjerknes forces [Crum, 1975], which will tend to force the bubble toward an acoustic antinode. Simultaneously, the bubble will also experience the buoyancy forces of gravitation which normally will be directed vertically upwards. Thus, under conditions that are not too difficult to obtain, it is possible to "acoustically levitate" a single bubble in the bulk of a liquid [Crum, 1980; 1983]. Under conditions that ARE reasonably difficult to attain, it is possible to see SL from this single bubble. We are investigating single bubble sonoluminescence (SBSL) by this levitation technique.

When we first studied acoustic levitation, our pressure amplitudes were typically on the order of 0.1 bar (0.01 MPa); accordingly, at these amplitudes the bubble behaved in a fairly linear fashion. However, in SBSL the pressures are over an order of magnitude larger and nonlinear effects are potentially important. We have discovered that we must account for these nonlinear effects. In some previous utilizations of this technique, for example, the acoustic field was calibrated from the measured position of the bubble. Thus, it is very important to understand the behavior of the levitated bubble, especially if it doesn't behave as one expects it to.

We investigated the effect of nonlinear bubble dynamics on the Bjerknes force and found some rather interesting aspects. Consider Fig. 1, which shows the magnitude of the instantaneous (obtained by numerical integration of the product of the time-varying volume and the acoustic pressure gradient) Bjerknes force on a bubble of radius 5 μm for a number of acoustic pressure amplitudes that are typical of those experienced by SBSL.

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Fig. 1. Instantaneous Bjerknes force on a 5 μm bubble. Note that as the pressure amplitude increases, the net force shifts from being almost entirely negative to having strong components in both directions.
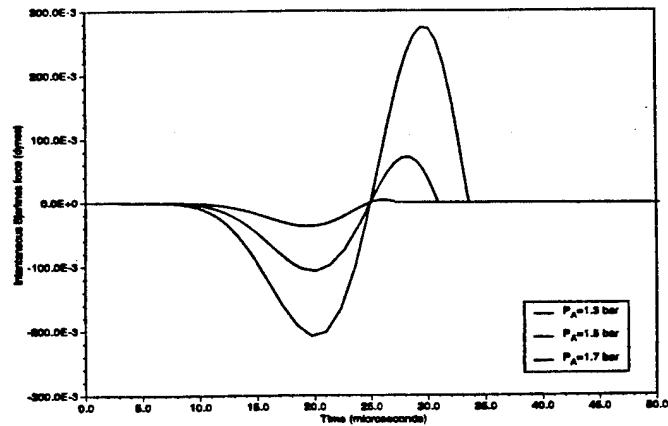
It appears that the reason the Bjerknes force develops a positive component is that the collapse phase of the bubble occurs at later and later times as the maximum amplitude of the bubble increases with increasing acoustic pressure. This behavior is shown on the following figure.

Fig. 2. Probable explanation for the trend shown in Fig. 1. As the pressure amplitude increases, the collapse point is delayed in time, extending the expanded phase of the bubble's motion in to the second half of the acoustic cycle-- which makes the Bjerknes force then positive. (Dashed line is the time varying acoustic pressure.)
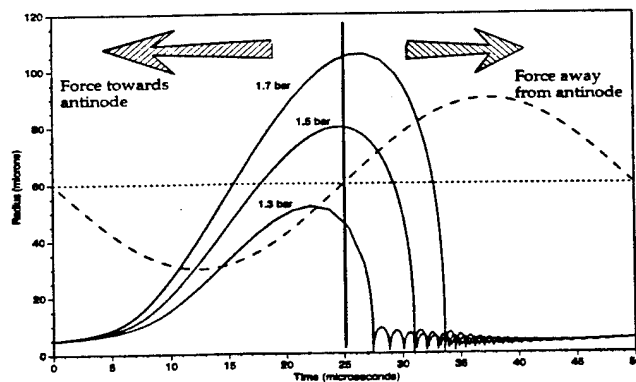
One of the consequences of this nonlinear Bjerknes effect is that the position of the levitated bubble does not follow a monatonic behavior as the pressure amplitude is increased. In fact, the bubble not only does not approach the antinode in a monatonic fashion, as it does in the linear case, but it actually turns around and moves away from the antinode. This behavior is shown in the following figure.

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Fig. 3. Variation in the vertical equilibrium position of a levitated bubble as a function of the applied acoustic pressure amplitude. The symbols (which are numerically computed values) are referred to the left axis, which corresponds to the position of the bubble. The solid line is referred to the right axis, which represents the acoustic pressure amplitude at the location of the bubble.
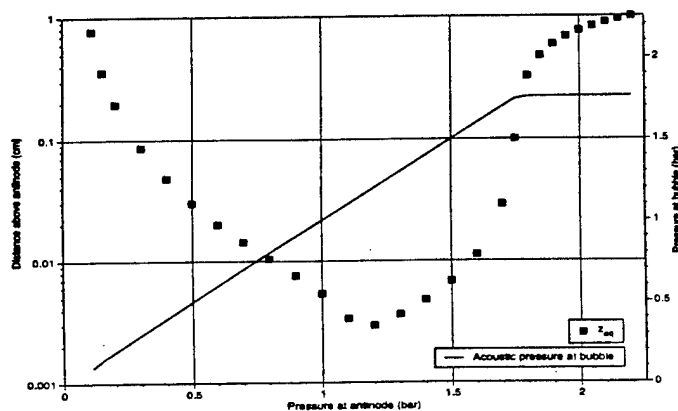
It is seen from Fig. 3 that there eventually the bubble will not sustain higher and higher pressures as the antinode pressure is increased--indeed, it saturates to a limiting value.

One can generalize this behavior by computing a "potential" surface, on which minima on the surface represent positions of stable equilibrium for the levitated bubble. Such a figure is shown in Fig. 4. below.

Fig. 4. A "potential" surface for bubble levitation. (For more details on the development and meaning of this surface, see Cordry [1995].
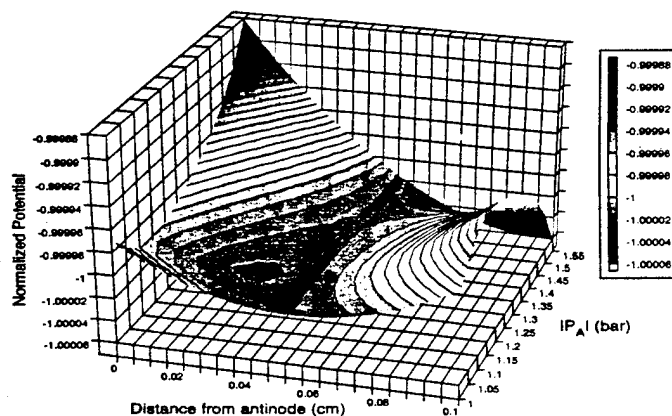
At first, we thought that perhaps this saturation was the reason that there is a limiting pressure for which one can drive a bubble undergoing SBSL. (As one increases the pressure amplitude the bubble suddenly disappears.) However, the transition observed in this case should be a gradual one, whereas SBSL extinction is sudden.

In an effort to confirm these predictions for the nonlinear Bjerknes effect, we performed some measurements for bubbles undergoing SBSL. These values are shown in Fig. 5.

Fig. 5. Comparison of computed values of the vertical equilibrium position with measurements for levitated bubbles undergoing SBSL. Note the correct trend but poor quantitative agreement. The open symbols are the measurements; the solid symbols are the computed values.
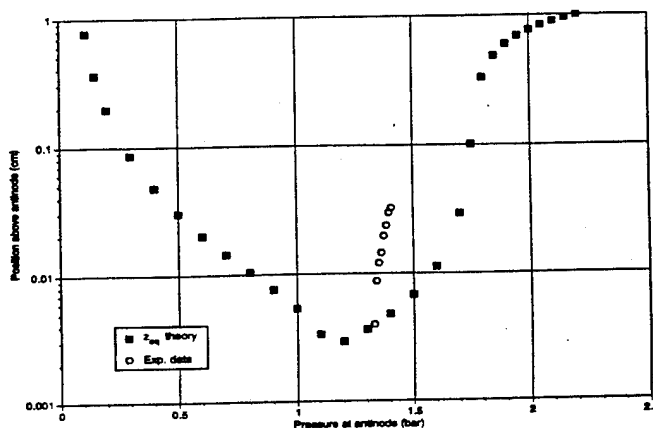
We considered various explanations for the lack of quantitative agreement with the predictions as shown in Fig. 5. Eventually we decided that the bubble was modifying (in a Heisenbergian sort of way) the acoustic field itself. Thus, we attempted a measurement of the field in the presence and absence of a levitated bubble. These measurements are shown in Fig. 6.

Fig. 6. Hydrophone response as a function of vertical position near the antinode for condition under which a bubble was either present (solid symbols) or not present (open symbols). Note the distortion produced by the presence of the bubble.
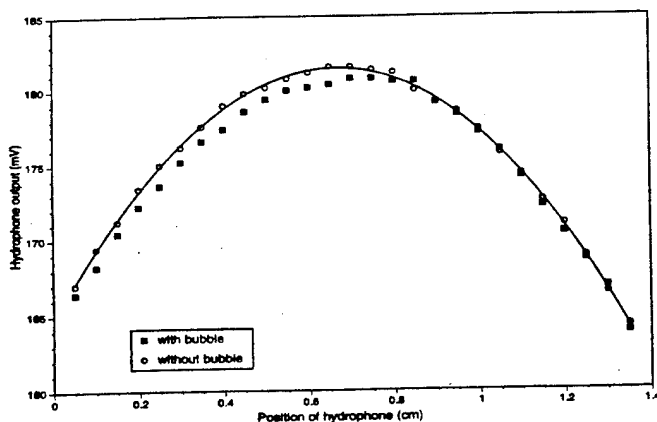
We next estimated the effective change in the wavelength (and thus the change in the acoustic pressure gradient) due to the bubble and discovered that if we used the measured acoustic pressure gradient, we could obtain excellent quantitative agreement. These results are shown in Fig. 7 below.

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Fig. 7. Comparison between measured (solid symbols) and computed (solid line) values of the vertical equilibrium position for levitated bubbles undergoing SBSL; in this case, the acoustic pressure gradient used in the calculations was the measured one.
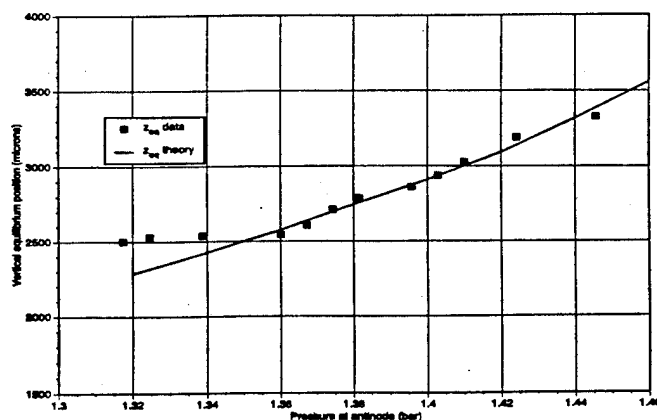
B. Acoustic versus electromagnetic outputs for a bubble undergoing SBSL.

We discovered that when a bubble was undergoing SBSL, the implosion causes a small acoustic field to be radiated. (Later, we discovered that the bubble didn't have to be luminescing for the field to be there.) We have used that information to learn something about the bubble and SBSL. Consider Fig. 8, which demonstrates the effect.

Fig. 8. The acoustic signature of a bubble undergoing SBSL. The top figure shows the manner in which a bubble grows and collapses during SBSL conditions; the middle figure shows the measured acoustic output as measured by a sensitive hydrophone placed near the bubble (note the little ripple near the time of bubble implosion); the bottom figure shows this radiated acoustic output when it is "high-pass" filtered.

8
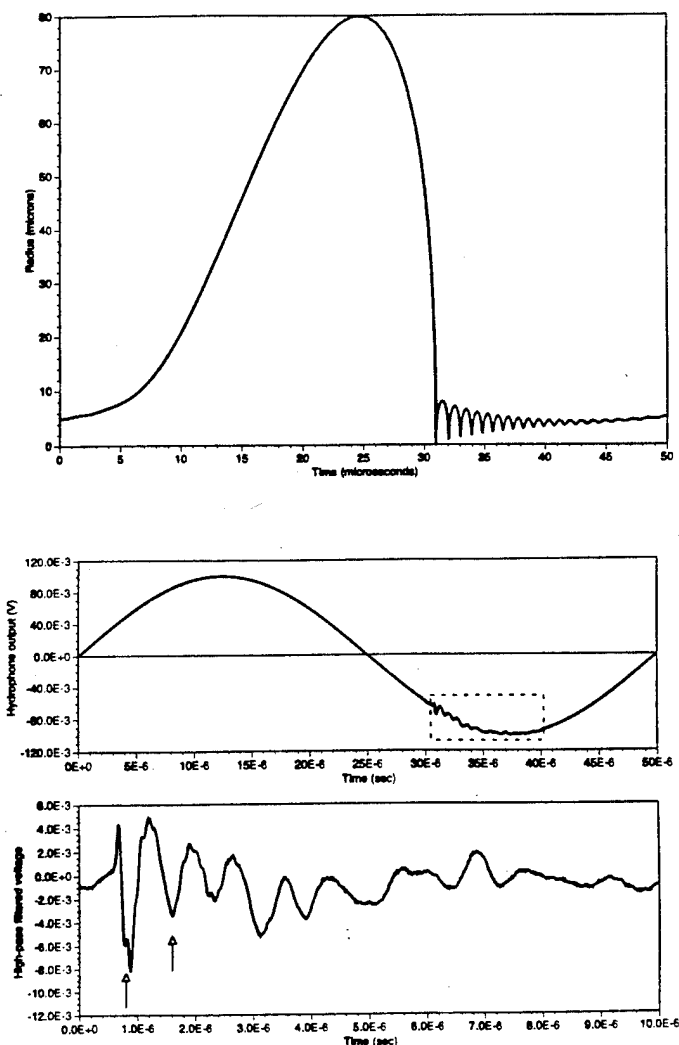
We have examined in some detail the acoustic and electromagnetic emissions for a variety of experimental conditions. One particularly illuminating sample of these measurements is shown in Fig. 9 below.
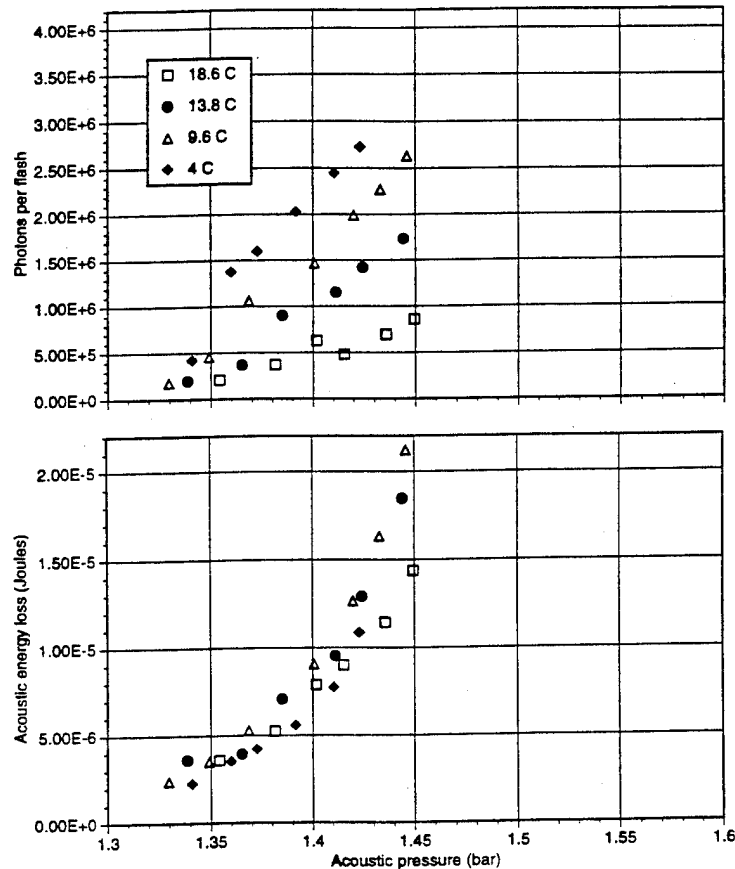
Fig. 9. Acoustic (bottom) and electromagnetic (top) emissions for a bubble undergoing SBSL for a variety of temperatures. In this case, the dissolved gas concentration was about 6% and the driving frequency was about 13 kHz.

There are some interesting observations that can be made from this figure. First, it is noted that higher levels of EM emissions are observed as the liquid temperature is reduced. Such a result has been observed earlier by Hiller, et al. [1992], and even earlier by Gaitan [Personal Communication]. Note also that the acoustic outputs, which are proportional to bubble dynamics--the more violent the collapse, the higher the radiated sound fields--don't change that much with temperature. There are two reasons for this: (a) the liquid properties (viscosity, surface tension, etc.) don't change that much with temperature, and (b) sound radiation tends to dominate the bubble damping--and thus the effects of the bubble's interior are not that important.

On the other hand, the EM outputs are strongly dependent on the internal bubble dynamics, particularly the vapor pressure and the amount of water vapor present in the interior

of the bubble. It is known that the vapor pressure has a strong dependence on the temperature, and this influence appears to be demonstrated in the EM output curves.

This figure is significant because it gives considerable support to the shock wave hypothesis for the origin of SL. Fig. 9 suggests that as one reduces the temperature, the bubble has little change in behavior from the bubble's surface outwards. What changes is the dynamics of the imploding shock wave within the bubble, which is greatly influenced by the vapor pressure of the liquid.

Summary

We have described a few aspects of our research accomplishments over the past year; the details are included in the publications. In particular, the recently completed dissertation of Sean Cordry has a wealth of new and exciting results, which should comprise the basis of at least three papers. Presumably, these will be finalized in the coming year.

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Barber, B. P. and Putterman, S. J., "Light scattering measurements of the repetitive supersonic implosion of a sonoluminescing bubble", Phys. Rev. Lett. **69**, 3939 (1992).

Cordry, S. M., "Bjerknes forces and temperature effects in single-bubble sonoluminescence", Ph. D. Dissertation, University of Mississippi, (1995).

Crum, L. A., "Bjerknes forces in a stationary sound field", J. Acoust. Soc. Am., **57**, 1363 (1975).

Crum, L. A., "Measurements of the growth of air bubbles by rectified diffusion", J. Acoust. Soc. Am. **68**, 203 (1980).

Crum, L. A., "The polytropic exponent of gas contained within air bubbles pulsating in a liquid", J. Acoust. Soc. Am. **73**, 116 (1983).

Gaitan, D. F., and Crum, L. A., "Observation of sonoluminescence from a single, stable, cavitation bubble in a water/glycerin mixture", in Frontiers of Nonlinear Acoustics, 12th ISNA, ed. by M. Hamilton and D. T. Blackstock, (Elsevier App. Sci. : New York); 1990, pp. 459-463.

Hiller, R., Putterman, S. J., and Barber, B. P., "Spectrum of synchronous picosecond sonoluminescence," Phys. Rev. Lett., **69**, 1182 (1992).

List of Publications, Patents, Presentations, and Honors

This report is appended immediately following.

OFFICE OF NAVAL RESEARCH
PUBLICATION/PATENTS/PRESENTATION/HONORS REPORT
for
1 June 1994--31 May 1995

R&T Number: 4k26966 – 01

Contract/Grant Number: N00014-93-1-0322

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Principal Investigator: Dr. Lawrence A. Crum

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a. Number of Papers Submitted to Referred Journal but not yet published: __2__

b. Number of Papers Published in Referred Journals: __2__
    (list attached)

c. Number of Books or Chapters Submitted but not yet Published: __1__

d. Number of Books or Chapters Published: __0__
    (list attached)

e. Number of Printed Technical Report & Non-Referred Papers: __3__
    (list attached)

f. Number of Patents Filed: __0__

g. Number of Patents Granted: __0__
    (list attached)

h. Number of Invited Presentations at Workshops or Prof. Society Meetings: __2__

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    (list attached, this might Include Scientific Soc. Awards/Offices,
    Promotions, Faculty Award/Offices etc.)__2__

k. Total number of Graduate Students and Post-Docs Supported at least 25%, this
    year on this contract,grant:
                        Grad Students __1__ and Post Docs _____

		[	Grad Student Female	__0__
		][		
How many of each are females or minorities?		][	Grad Student Minority	__0__
(These 6 numbers are for ONR's EEO/Minority		][		
Reports; minorities Include Blacks, Aleuts		][	Grad Student Asian e/n	__0__
Amindians, etc and those of Hispanic or		][		
Asian extraction/nationality. This Asians		][	Post-Doc Female	__0__
are singled out to facilitate meeting the		][		
varying report semantics re "under-		][	Post-Doc Minority	__0__
represented")		][		
		][	Post-Doc Asian e/n	__0__

a. List of papers submitted to referred journals but not yet published.

"Nonlinear coupling between the surface and volume modes of an oscillating bubble", Y. Mao, L. A. Crum and R. A. Roy, J. Acoust. Soc. Am. (accepted for publication, May 1995).

"Comments on the evolving field of sonochemistry by a cavitation physicist", L. A. Crum, (accepted for publication in Ultrasonics (Sonochemistry) .

b. List of papers published in referred journals.

"Sonoluminescence", L. A. Crum, Physics Today, September, 1994.

"Sonoluminescence", L. A. Crum and R. A. Roy, Science, (Perspectives) **266**, 233-234 (1994).

c. List of book chapters submitted but not yet published.

"Sonoluminescence", S. Cordry and L. A. Crum, to be published in Luminescence in Solids and Liquids, Dr. R. Vij, ed., (Plenum Pub. Co.: scheduled for 1995).

e. List of papers published in non-referred journals.

"Single bubble sonoluminescence", L. A. Crum, Proceedings Fifth Western Pacific Regional Acoustics Conference, Seoul, Korea, **1**, 17-25 (1994).

"Bubbles hotter than the sun", L. A. Crum, New Scientist, **146**, 36-41 (1995).

"Sonoluminescence", L. A. Crum, Parity, **10**, 13-22 (1995). (Japanese translation of Physics Today article).

H. List of invited presentations at professional society meetings.

"Single bubble sonoluminescence", presented at the Fifth Western Pacific Regional Acoustics Conference, Seoul, Korea, 23-26 August, 1994.

"Sonoluminescence", with S. Cordry, presented at the 128th meeting of the Acoustical Society of America", Austin, TX, November (1994).

I. List of contributed presentations at professional society meetings.

"A novel technique for measuring the maximum radius of a sonoluminescing bubble, with S. M. Cordry, presented at the 127th meeting of the Acoustical Society of America, Cambridge, MA, June (1994).

"Mass diffusion in spark-induced vapor bubbles", with J. S. Allen, M. A. Averkiou, C. M. Young and G. R. Hess, presented at the 128th meeting of the Acoustical Society of America, Austin, TX, November (1994).

"Acoustic modeling of plasma-induced vapor bubbles", with G. R. Hess, A. E. Rodriguez, N. K. Winsor, C. M. Young and R. F. Stellingwerf, presented at the 128th meeting of the Acoustical Society of America, Austin, TX, November (1994).

"Nonlinear bubble oscillations and Bjerknes forces", with S. M. Cordry and R. A. Roy, presented at the 129th meeting of the Acoustical Society of America", Washington, DC, May (1995).

j. Honors/Awards/Prizes

• L. A. Crum was selected as the winner of the ASA award for popular articles on acoustics by a scientist.

• L. A. Crum was elected an associate member of the International Commission on Acoustics.

Nonlinear coupling between the surface and volume modes of an oscillating bubble

Yi Mao

Department of Physics and Astronomy, University of Mississippi, University, MS 38677

Lawrence A. Crum and Ronald A. Roy

Applied Physics Laboratory, University of Washington, Seattle, WA, 98105

An experimental study was conducted of the nonlinear coupling between the surface and volume modes of an oscillating bubble. Through this coupling, the surface modes of a bubble can produce monopole sound radiation, which has a higher radiation efficiency than the surface modes. A hydrophone and a hypodermic needle, connected to an air supply, were submerged in water in a small ($7.1 \times 7.1 \times 7.7$ cm^3) sealed cell that was also connected to a regulated vacuum system for control of the ambient pressure. The sound radiation produced by releasing a bubble from the needle was monitored by a hydrophone and displayed on a digital oscilloscope. Two high-speed video cameras simultaneously recorded the radial motion of the bubble and the sound radiation trace as displayed on an analog oscilloscope. At low ambient pressures (i.e., a few cm–Hg), it was observed that after the bubble creation sound died out, a sound of the same frequency but with a lower and relatively constant magnitude followed. Therefore, we believe that these subsequent acoustical emissions are evidence of the coupling between the surface and the volume modes of the bubble. Observation of a constant phase angle between the surface oscillations of the bubble and the radiated sound suggests a causal relationship.

Introduction

Some of the earliest studies of noise in the ocean were published in 1948 by Knudsen, Alford and Emling. Since then, much progress has been made toward the understanding of ocean ambient noise. We now know that many sources contribute to ocean ambient noise. Some of these are rain (Pumphery, et al., 1989; Scrimger, et al., 1989), hail, snow (Scrimger, et al., 1987; Crum, et al., 1992), wind and breaking waves (Banner, et al., 1988), and capillary waves (Kolaini, et al., 1993; 1994a). The noises from these sources are all bubble-related. The basic physical mechanism through which a bubble generates acoustical radiation is a fundamental question that has important consequences in many fields, but especially in oceanography.

Mathematically, the oscillation of a bubble can be treated using linear theory as a superposition of its normal modes (Lamb, 1932). Each normal mode is associated with a Legendre polynomial, say $P_l(\cos\theta)$, where l is the order of the polynomial. The mode corresponding to the lowest order Legendre polynomial ($l=0$) is a monopole. It is the only one involving the oscillation of the bubble volume. Therefore, this mode is often called the volume mode or "breathing mode". All higher order modes are referred to as shape modes (or surface, distortion, or asymmetric modes). Each mode oscillates at its own resonance frequency which is often called its natural or fundamental frequency. The sound field of the lth order mode decays with the distance r from the bubble as $r^{-(l+1)}$. The monopole radiation is dominant in the far field, whereas the shape mode radiation is less significant and often totally ignored in the far field. In the ocean, newly created bubbles, the principal origin of bubble-related noise, are normally deformed from a spherical shape during the generation and injection process. Thus, surface waves of relatively large amplitudes exist on these bubbles. Since equations of fluid dynamics are intrinsically nonlinear, an important question is whether these shape oscillations,

by coupling nonlinearly to the monopole radiation, provide a significant contribution to the far field acoustical radiation.

Several theoretical studies (Longuet-Higgins, 1989a, 1989b, 1991, 1992; Ffowcs Williams and Guo, 1991) suggest a significant contribution to the ocean ambient noise through this nonlinear coupling. Also, there exists some experimental evidence in support of this suggestion. For example, in the laboratory breaking wave experiment of Medwin and Beaky's (1989), the variation of the damping constant of the bubble-related noise was interpreted by Longuet-Higgins (1992) to be a consequence of this nonlinear interaction. Another example is Kolaini's recent investigation [Kolaini, 1994b] of the interaction between a bubble and turbulence generated by a jet of water. In this experiment, a liquid jet, with a speed comparable to that of an ocean current, was used to create a large deformation of a bubble. For the interesting case in which the bubble was distorted but not fragmented, it still emitted a strong monopole signal (Fig. 1). This experiment suggests that because there are abundant surface mode excitations in the ocean, "adult" bubbles can be stimulated into acoustical emissions via a mode-coupling mechanism. Of course, these interpretations for both Medwin and Beaky's and Kolaini's experiments are not conclusive; interpretations other than nonlinear mode coupling are possible. For example, it is possible that the volume mode was excited by the breaking waves or the liquid jet. In either example, there was no way to distinguish between a direct and indirect stimulation of the volume mode. In this paper, we present detailed experimental evidence of the existence of the nonlinear mode coupling phenomenon (Mao, et al., 1992; Mao, 1993).

Experimental Approach

In our experiment, we used a hypodermic needle immersed in water to create a bubble. Not only was this method quite simple and direct, but also the excitation of the bubble occurred only at the moment for which the bubble left the tip of the needle. Both surface and volume modes were simultaneously excited at the moment the bubble was detached from the needle. Our task was to find the induced monopole radiation.

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Since the amplitude of this radiation is expected to be small, we need to create favorable conditions so that the effect is large enough to be observed in a laboratory. First of all, a resonance condition, i.e., the frequency of the volume mode is twice that of the surface mode (Longuet-Higgins, 1989a), is desired. Secondly, the amplitude of the surface mode to be coupled to the volume mode should be excited at a relatively large amplitude. Finally, because the amplitude of the induced volume mode radiation is quite small, the ideal situation would be one in which the bubble had only shape modes, without the accompanying (and, for our interests, contaminating) initial volume mode. However, when a bubble is released from a needle, a volume mode is inevitably excited in addition to the surface modes. The amplitude of this initial volume mode can be at least one order of magnitude larger than that induced through surface-mode coupling. Thus, any additional (and subsequent) contribution to the volume mode by the surface modes will be totally "masked" and this mode indistinguishable. It is desirable, therefore. that this "masking" effect be significantly reduced or entirely eliminated. We seek ways of reducing this initial-volume-mode-masking.

When the bubble leaves the needle, a number of surface modes are excited. However, a low-order surface mode usually has a larger amplitude simply because a low-order surface mode requires less variation along the surface of the bubble. Therefore, the involvement of a low-order surface mode in the mode coupling will greatly enhance the effect .

The natural frequencies ω_l of a monopole and a surface mode can be calculated by the following formula:

$$\omega_l^2 = \begin{cases} \dfrac{3\gamma p_0}{\rho a^2} - \dfrac{2\sigma}{\rho a^3}, & l = 0 \\[3mm] (l-1)(l+1)(l+2)\dfrac{\sigma}{\rho a^3}, & l > 0 \end{cases}, \tag{1}$$

where p_0 is the ambient pressure, σ is the surface tension, a is the radius of the bubble, γ is the ratio of the specific heats, and ρ is the liquid density. The coupling between a surface mode and a volume mode reaches maximum at resonance, viz.,

$$\omega_0^2 = 4\omega_l^2, \qquad (l = 2,3,...). \qquad (2)$$

At atmospheric pressure $p_0=1$ atm, for a surface tension $\sigma=75$ dyne/cm, and a typical bubble size $a=0.1$ cm, the order of the surface mode which satisfies the resonance condition (2) will be as high as 11. In order to involve a low-order surface mode in resonance condition (2), we need to adjust some parameters involved in (1). One of the parameters is the bubble radius a. The natural frequency of a volume mode changes with the bubble size a as a^{-1} when the radius a is not too small, while that of a surface mode varies as $a^{-3/2}$. Hence, decreasing the bubble size would achieve the goal. However, for the second and third order surface modes to meet the resonance condition (2), the required bubble radius a would be 81 μm and 278 μm, respectively, provided all other parameters are kept unchanged. A bubble of such a small size is difficult to create by our chosen method (i.e., by releasing it from a needle). We also found that a small bubble ($a<0.13$ cm) released from a needle had a very small initial surface and volume mode excitation, not to mention that a small bubble has a low radiation efficiency. Thus, decreasing the bubble size is not a desirable approach. Another parameter is the surface tension σ. Increasing the surface tension will move the natural frequency of a volume mode down and that of a surface mode up, and therefore, cause a low-order surface mode to match the volume mode. Since most surfactants decrease rather than increase the surface tension, this option is not feasible either.

The obvious choice is to lower the ambient pressure. Lowering the ambient pressure will reduce the natural resonance frequency of the volume mode but have no influence on the natural resonance frequencies of surface modes. Furthermore, when the ambient pressure p_0 decreases, the polytropic index γ will decrease. This change results in an additional decrease in the volume mode frequency. An unanticipated advantage that occurs when the pressure is lowered is that the

"masking" effect can be significantly reduced. As the ambient pressure is lowered, the percentage of vapor within the bubble increases and so does the damping associated with the vapor condensation-evaporation process. Being sensitive to volume fluctuation, the vapor condensation-evaporation process has a greater effect on the damping of the volume mode than on the surface modes. Consequently, the enhanced damping of the initial volume mode and the better coupling of the volume mode with lower-order surface modes enable the nonlinear mode-coupling phenomenon to be observed.

The experimental arrangement (Fig. 2) consisted of an experimental cell and three measuring systems: a vacuum regulation system, a data acquisition and signal display system, and an optical image processing system. The experimental cell (Fig. 3) was an airtight sealed cell approximately 7.1 cm x 7.1 cm x 7.7 cm in size. The side walls of cell were made of Plexiglas and the top and bottom walls were brass. In the top and bottom walls, there were inlets for filling water and for supplying air for the needle, and an outlet for connecting the cell to the vacuum regulation system. At the center of the bottom, a needle was mounted vertically. A miniature hydrophone (Brüel &Kjær, Type 8103) was positioned 2 cm away from the needle and 0.5 cm above the tip of the needle. The relatively heavy cell rested on a sponge cushion for vibration isolation.

The vacuum regulation system consisted of a U-tube mercury manometer for reading the pressure difference between the inside and outside of the cell, a vacuum regulator for controlling the pressure inside the cell, and an aspirator pump for evacuation. The absolute pressure inside the cell was obtained through the readings of a barometer and the manometer.

The data acquisition and signal display system utilized a hydrophone, a preamplifier, a filter, a digitizing oscilloscope and an analog oscilloscope. The miniature hydrophone sealed inside the cell was used to detect the sound emitted by a bubble from the needle. The electrical signal from the hydrophone was amplified (Brüel &Kjær, Type 2635), filtered (Krohn-Hite, Model 3202), and displayed on both the digitizing oscilloscope (Hewlett-Packard, Model HP-

51089A) and the analog oscilloscope (Tektronix, Model 2445). The digitizing oscilloscope had the capability to store the signal data on a disk for later data processing. The signal trace on the screen of the analog oscilloscope was used for real time display as described in the following paragraph.

The optical image processing system was designed to determine the temporal correlation between the bubble motion and the emitted sound. The system consisted of two high-speed video cameras and an image processor (Kodak Ekta Pro 1000 Processor). The two cameras simultaneously recorded, at a speed of 1000 frames/second, the motion of the bubble and the acoustical signal (filtered hydrophone voltage) displayed on the analog oscilloscope. The images for the motion of the bubble and the sound trace were fed into the image processor which combined the two images side by side and recorded them on tape. A monitor could display a real-time image or a recorded image.

The cell was partially filled with degassed water; there was a small gap between the water surface and the top inner wall of the cell. A vacuum (about 2 cm-Hg) was then applied to the cell to rid the system of the bubbles attached to the inner walls, the hydrophone and the needle. (Sometimes, a gentle shake of the cell was helpful). This vacuum was maintained for two or three days before the experiment began. The needle tips were ground flat and needles of several sizes were utilized. During the experiment, bubbles were released individually. The interval between two bubbles was long enough so that any disturbance made by the second bubble would not interfere with the sound emitted by the first one.

Experimental Results

A.   General Observations

Three different sizes of needles were used in the experiment. The outer diameters of these needles are 0.30 mm, 0.89 mm and 1.62 mm respectively. Bubbles from the 0.30 mm needle displayed neither an initial volume mode nor an initial surface mode excitation. No sound could be measured by the hydrophone after they left the needle. High-speed video images of these bubbles showed that their shape, after being detached from the needle, was nearly a perfect sphere, without any surface oscillation. Video images of bubbles released from the 0.89 mm needle showed both an initial volume mode excitation and a surface mode excitation at pressures below about 12 cm-Hg. For pressures above 12 cm-Hg, there were no initial disturbances as was the case with the 0.30 mm needle. For the entire pressure range (from 2 cm-Hg to 76 cm-Hg), bubbles released from the 1.62 mm needle were observed to have initial volume and surface mode excitations. Bubble sizes were estimated by measuring the image sizes of both the bubble and the needle and scaling relative to the actual sizes of the needles.

Fig. 4 shows the dependence of the bubble diameter upon the ambient pressure for bubbles produced by needles of outer diameters 0.89 mm and 1.62 mm. For the 1.62 mm needle, the bubble diameter is almost constant over the entire pressure range. For the 0.89 mm needle, the bubble size remains constant until the pressure drops to 25 cm-Hg and below that the bubble diameter increases dramatically. It was found that the initial mode excitations were closely related to the bubble size. Neither volume nor surface mode excitations were observed for bubble diameters less than 2.65 mm (the experimental point labeled "NS"), whereas, for a bubble diameter larger than 2.8 mm (the experimental point labeled "S") measurable sound was radiated. The video images showed that a small bubble was formed by closing itself before it left the needle and a large bubble was formed by closing itself upon leaving the needle. Thus, the large bubble had significant initial distortion which led to subsequent noise emission. Because of these two different bubble creation mechanisms, it appeared that bubbles released from a needle emit sound only if the bubble diameter exceeds a threshold. This threshold probably varies with the conditions (smoothness, contamination, shape, etc.) of the needle tip. In this experiment, the threshold diameter was about 2.8 mm. The natural frequency of volume mode was obtained

through a FFT analysis of the sound signal. Because of the limited duration of the signal, the resolution of the FFT affected the precision of the frequency measurement. At low pressures, the frequency of the volume mode was obtained by measuring the period of the signal directly on the oscilloscope rather than through use of the FFT. With the help of this complementary method at low pressures, the precision of the measurement for the whole pressure range was within 6%.

B.   The Volume Mode Induced by the Surface Modes.

At low ambient pressures (a few centimeters of mercury), we have found strong evidence for the presence of surface-to-volume mode coupling in an oscillating bubble. Fig. 5, which shows the acoustic radiation from a bubble released from the 0.89 mm diameter needle at a pressure of 4.05 cm-Hg, is an example of this evidence.

With the use of the high-speed video system, we can examine the correlation between the sound signal and the motion of the bubble, and thus differentiate between initial and induced volume mode radiations.

In our experimental system, at low pressures, a bubble could radiate sound while it was forming on the needle tip. The bubble was initially created when some of the air suddenly rushed out of the orifice of the needle. The bubble continued to grow at a decreased rate and finally reached a size beyond which the surface tension along the rim of the opening could no longer withstand the buoyancy force of the bubble; at this point, it left the needle. We call the noise made by the bubble as it was initially created the "pop-out noise". Subsequently, when the bubble left the needle, it was again stimulated into radiating sound. We call the noise that was emitted when the bubble detached from the needle the "pinch-off noise". This particular oscillation had volume as well as surface mode components. As noted before, the low-order surface modes were more abundant. The "pinch-off noise" carried principally the signature frequency of the volume mode.

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At low ambient pressures, because of increased damping, the "pinch-off noise" decayed very rapidly, lasting only a few cycles. After it died away, the hydrophone indicated a quiet interval of a few milliseconds, during which no sound above the random background noise was detected. However, following this interval, a sound of a similar frequency reappeared. Because the frequency of this emission was identical to that of the "pinch-off noise", this sound must be due to the volume mode. We believe that this subsequent signal was the sound radiated by the volume mode which was reinvigorated by the surface-to-volume coupling. Thus, we call this sound the "mode-coupling noise".

We can observe from Fig. 5 that the delay of the "mode-coupling noise" from the "pinch-off noise" is approximately 20 ms. By assuming that the sound velocity in water at low pressure is 1400 m/s, we would expect that a wall reflection with this time delay would be located 14 m $(=\frac{1}{2}(1400 \,^m\!/_s \times 0.020s))$ away from the bubble. However, the dimensions of the experimental cell were of the order of 10 cm. Thus, it was not possible for this low frequency sound to be an echo of the "pinch-off noise." We observed from the video images that the bubble surface modes were clearly active during this entire period. Careful examination of the video images revealed that, at this low pressure, the bubble radiated two complete acoustical cycles for each surface-mode cycle. Fig. 6 represents the video images, showing the correlation between the bubble shape oscillation and the "mode-coupling noise". (The actual video frames do not produce clearly enough to be of publication quality.)

The behavior of the "mode-coupling noise" with changing ambient pressure fits closely the properties one expects for a surface-mode-induced-volume-mode. Fig. 7 shows the acoustical signals emitted by bubbles released from the 1.62 mm diameter needle at various ambient pressures. In this figure, we display a range of ambient pressures from about 55 cm-Hg down to a few centimeters of mercury. The radiated acoustical signals for pressures in the excess of 55 cm-Hg are all approximately the same. The first two plots (for pressures at 54.65 cm-Hg and 34.75 cm-Hg) show no apparent evidence of mode-coupling noise. The volume mode at these

pressures will be in resonance with high-order surface modes, which have a negligibly small amplitude. In addition, the damping of the volume mode is too small. As a consequence, even if there is a small conversion of surface mode energy to the volume mode, the "masking" effect will overwhelm any evidence of the latter. As the ambient pressure decreases, there is increased damping of the volume mode. Meanwhile, the coupling between the volume mode and the large-amplitude low-order surface modes gradually increases. The "mode-coupling noise" becomes stronger and stronger as the pressure is continually reduced. At this point there is optimal coupling between the low-order surface modes and the volume mode.

C.   The Interaction between the Volume Mode and the Surface Oscillation.

In the previous section, we have presented experimental evidence of the volume mode excited by the surface oscillations. In this section, we will show that some of the energy of the volume mode can also be transferred to the surface oscillations through a nonlinear interaction.

Longuet-Higgins demonstrated that resonance coupling between a volume mode and a surface mode could be another damping mechanism for the volume mode. He employed a set of equations which was for the near-resonance interaction and with damping terms due to all damping mechanisms (thermal, viscous, radiation) except the resonance damping. His numerical results are reproduced in Fig. 8. The vertical axis is the envelope of the absolute value of the amplitude of the volume mode for a logarithmic scale; the horizontal axis is the "slow" time multiplied by the circular frequency of the volume mode (Longuet-Higgins, 1992). The negative of the slope of the curves is proportional to the damping of the volume mode. A negative slope at a point on the curve means a positive damping constant (the energy stored in the volume mode decreases); a positive slope at a point on the curve implies a negative damping constant (the energy stored in the volume mode increases). If there were no resonance damping involved, the damping constant would be a positive constant (the slope would be negative and the amplitude of the oscillation would decrease constantly). However, when resonance damping is involved, the damping can be either positive or negative. Part of the energy of the volume mode can be

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transferred to the surface mode and, subsequently, the surface mode will then pump some of the energy back to the volume mode. The consecutive plots in Fig. 8 reflect the effects of the surface mode damping upon the total volume-mode damping. For a small amount of surface mode damping, the energy from the volume mode is not totally dissipated by the surface mode and a portion of this energy is sent back to the volume mode so that the curve oscillates (see, for example, Fig. 8a). On the other hand, for a large amount of surface mode damping, the volume mode does not get much energy back from the surface mode and the curve is a straight line (see, for example, Fig. 8d).

Because the data sets for the 1.62-mm diameter needle include complete information over an entire range of ambient pressures and for a constant bubble size, these data sets are used to make a comparison with Longuet-Higgins' theory. First, we extract all points with a maximum absolute value of sound pressure from each half cycle of sound emission. Then, the newly formed data are rescaled by dividing the sound pressure with the maximal value of the newly formed data. Finally, the rescaled sound pressure (natural logarithm) is plotted versus the time. We show the results in Fig. 9. Comparing Fig. 8 and Fig. 9, we see that the first two plots of Fig. 9 (pressure at 54.65 and 34.75 cm-Hg) have a similar structure to Fig. 8d, the plot for the pressure at 24.25 cm-Hg is similar to Fig. 8c, and the plot for the pressure at 10.25 cm-Hg is similar to Fig. 8a.

The interaction between a volume mode and a surface mode depends on several parameters. One parameter is the "bandwidth parameter" defined by Longuet-Higgins (1992) to measure how far the volume and the surface modes are off resonance. Another parameter is the initial amplitude of the surface mode. If there is no initial surface mode, no interaction will occur thereafter. This can be seen in Eq. (11) of Longuet-Higgins' article (1992). If the amplitude of the surface mode C_n is equal to zero, the differential equations for the amplitudes of the modes are not coupled. A large amplitude of the initial surface mode will result in a strong interaction. Still another parameter is the ratio of the ordinary damping constant of the volume

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mode to that of the surface mode. Fig. 8 only shows the effect of this last parameter on the pattern of the envelope of the sound. The experimental results are much more complicated than the idealized theory because more than one surface mode is involved and the relevant parameters are all changing with the ambient pressure. In spite of this complication, our results are qualitatively in agreement with this theory and more importantly, the underlying physics is revealed. The interaction of the volume and surface modes does exist and increases with a corresponding decrease in the ambient pressure. The exchange of energy between the volume and surface modes causes the volume mode damping coefficient to oscillate.

Relevance to Ocean ambient Noise

With reference to the more general questions, there are several reasons that suggest that the surface modes of bubbles may make a contribution to the total ambient noise of the ocean.

First, in the far field, the sound pressure of the surface-mode-induced volume mode is much larger than the sound pressure emitted directly from the surface mode. We use Eq. (3) [Longuet-Higgins, 1991, Eq. (4.9)] as the sound pressure for the induced volume mode because, according to this theory, Eq. (3) represents the minimal value of the sound pressure of an induced volume mode regardless of what the damping of the bubble oscillation would be,

$$(p')_{t=0} = -\frac{3\varepsilon^2(n-1)(n+2)}{4(2n+1)}\frac{\sigma}{r}. \qquad (3)$$

where n is the order of a surface mode and ε is a small perturbation parameter which is equal to the ratio of the amplitude of a surface mode to the bubble radius a. By using Eqs. (2.1-2.4) from the same reference, and $C_n(0) = 1$ and replacing $S_n(\theta, \varphi)$ with its maximum value 1, we have the expression for the sound pressure emitted directly by the nth order surface mode

$$(p'_n)_{t=0} = -\rho\frac{\partial(\varepsilon a \phi_n)}{\partial t} = -\rho\varepsilon a \frac{\omega_l^2}{n+1}\frac{a^{n+2}}{r^{n+1}} = -\varepsilon\frac{2(n-1)(n+2)\sigma a^n}{r^{n+1}}. \qquad (4)$$

The ratio of $(p')_{t=0}$ to $(p'_n)_{t=0}$ is found to be

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$$R_{0,n} = \frac{3\varepsilon}{8(2n+1)}\left(\frac{r}{a}\right)^n, \qquad (n=2,3,4...), \qquad (5)$$

which is independent of the surface tension. If we choose the ratio of the surface disturbance to be $\varepsilon=0.1$, the bubble radius $a=1.5$ mm, and the distance between the center of the bubble and a point where the sound is measured to be $r=10$ cm, we can calculate the ratio given in Eq. (5). These results are shown in Fig. 10. For the smallest value, n=2, the ratio $R_{0,2}$ is 33; for the next, n=3, the ratio $R_{0,3}$ is 1587. This ratio increases exponentially with the order of the surface mode. Thus, it is seen that the far field sound produced by a surface mode via mode coupling is much more effective than a surface wave radiating by itself.

Secondly, the surface modes which can be in resonance with the volume mode at atmospheric pressure could be excited in the ocean. In this study, the method employed to create a bubble has a disadvantage: neither surface nor volume modes can be excited for a small bubble. Furthermore, for a large bubble (a few millimeters in diameter), a high-order surface mode which satisfies the resonance condition has a negligible amplitude. Because of this disadvantage, we needed to resort to lowering the ambient pressure to meet the resonance condition. In the ocean, however, bubbles in turbulent flow, or in breaking waves, or near a fast moving object such as a propeller could have surface mode excitations even if their sizes were small. For a large bubble, high-order surface modes could be excited to a significant amplitude. In fact, low-order surface modes of a small bubble and high-order surface modes of a large bubble need the same scale of the space variation of a turbulent flow to be excited. Therefore, a bubble in a flow which is violent enough would radiate sound via the induced volume mode.

Finally, it is known that sound is momentarily radiated by bubbles during their creation process--the "infant wail". However, "adult bubbles" that were constantly excited into surface modes in the ocean would have a long-term cumulative effect in their contribution to the ambient noise. For a single excitation of a surface mode from bubble creation, for example, the induced volume mode does not make a significant contribution to the ambient noise. However, for a

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bubble which is in a turbulent field or in a breaking wave, the flow should continuously excite the bubble's surface modes. The induced volume mode, which has a steady energy supply from the prolonged excitation of the surface mode, could then grow in amplitude without an energy limitation, as noted by Ffowcs Williams and Guo (1991). Of course, the relative ratio of "infant" versus "adult" bubbles in the total bubble-related ambient noise spectrum is still to be determined.

Summary and Conclusions

The principal results of this study are as follows:

(1) Experimental evidence is presented of surface-to-volume mode coupling in oscillating bubbles.

(2) Evidence is also presented that demonstrates that surface-volume mode interaction can lead to oscillatory variation in the damping of the volume mode.

(3) It is suggested that under certain conditions, "adult" bubbles, stimulated into surface oscillations, could contribute to the total bubble-related ambient noise in the ocean.

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Captions of Figures.

Fig. 1. The sound radiated from a gas bubble in a fully developed turbulence jet. (a) The initial "pinch-off" noise when the bubble released from a needle. (b) The noise radiated by the bubble when it is deformed by the jet. (c) The FFT power spectrum of (a) and (b) indicates that this "adult" bubble was stimulated into sound radiation at its (natural) resonance frequency. (These previously unpublished data were preciously provided by A.R. Kolaini, 1994b)

Fig. 2. Block diagram of the experiment for measuring the sound radiation of the volume mode induced by surface modes through nonlinear interaction.

Fig. 3. Detailed view of the arrangement inside the cell for measuring the sound of the volume mode induced by a surface mode.

Fig. 4. Experimental data representing the dependence of bubble average diameter upon the ambient pressure when released from a hypodermic needle of the indicated sizes. "S" and "NS" refer to "sound" and "no sound" conditions; for the 1.62 mm diameter needle, sound was radiated by all bubble released.

Fig. 5. Radiated acoustic pressure from a bubble released from the 0.89 mm diameter needle at a pressure of 4.05 cm-Hg. The circled portion of the signal is due to radiation from the induced volume mode.

Fig.6. Reconstructed drawing from video images showing the correlation between the shape oscillation and the sound emission from the induced volume mode when the sound emission is relatively large. It should be noted that one full cycle of a shape oscillation results in two cycles of volume oscillation.

Fig.7. Acoustic emissions from bubbles released from a 1.62 mm diameter needle at various pressures. Note that the amplitude of the "mode-coupling" noise increases as the ambient pressure decreases, suggesting an approach to resonance conditions.

Fig.8. Theoretical calculation of the influence of surface oscillations on the volume-mode damping constant. Here, the amplitude envelope ϵC_0 of the volume mode was plotted against slow time $\omega\tau$: (a) $\beta/\omega=0.01$, $\beta_v/\omega=0.01$; (b) $\beta/\omega=0.01$, $\beta_v/\omega=0.02$; (c) $\beta/\omega=0.01$, $\beta_v/\omega=0.10$; (d) $\beta/\omega=0.01$, $\beta_v/\omega=1.5$, where β and β_v are respectively the volume and surface mode damping constants, and w is the circular frequency of the volume mode [from Longuet-Higgins, (1992)].

Fig. 9. Experimental evidence of the influence of surface oscillations on the volume-mode damping constant. Here, the natural logarithm of the maximum absolute value of acoustical emissions shown in Fig.7 is plotted against time. The slope of the curves is the damping constant. The interaction of surface and volume modes causes the curves to oscillate. Compare with the theoretical calculations shown in Fig.8.

Fig. 10. The ratio of the sound pressure of the volume mode induced by a surface mode to that emitted directly by the surface mode at a distance 10

cm away from a bubble of 1.5 mm radius. Note that this ratio increases
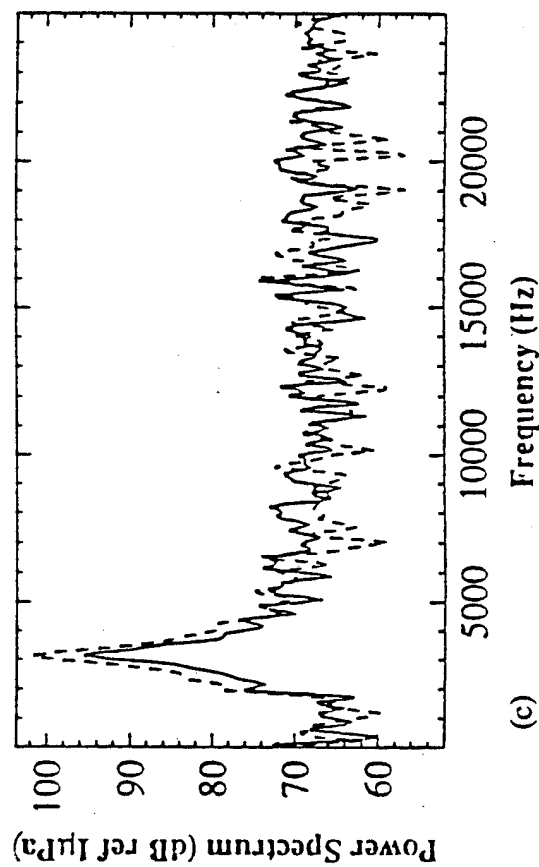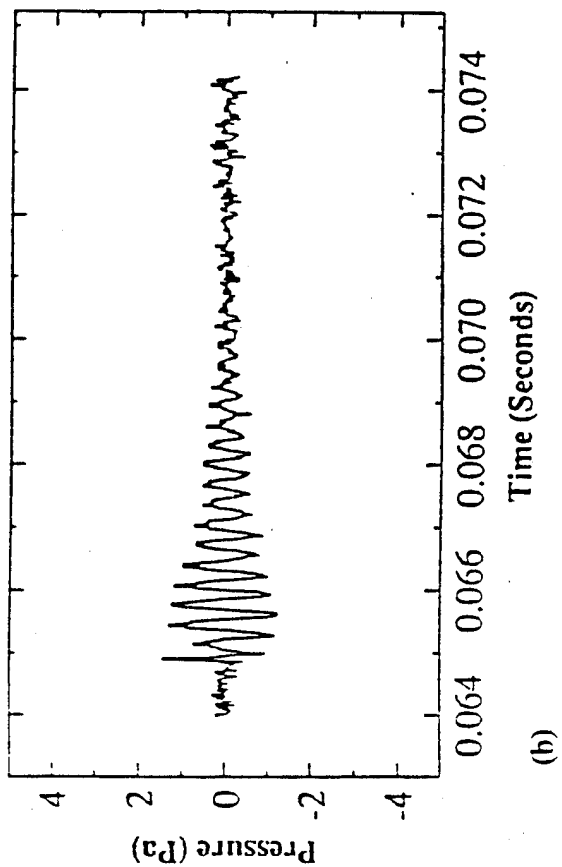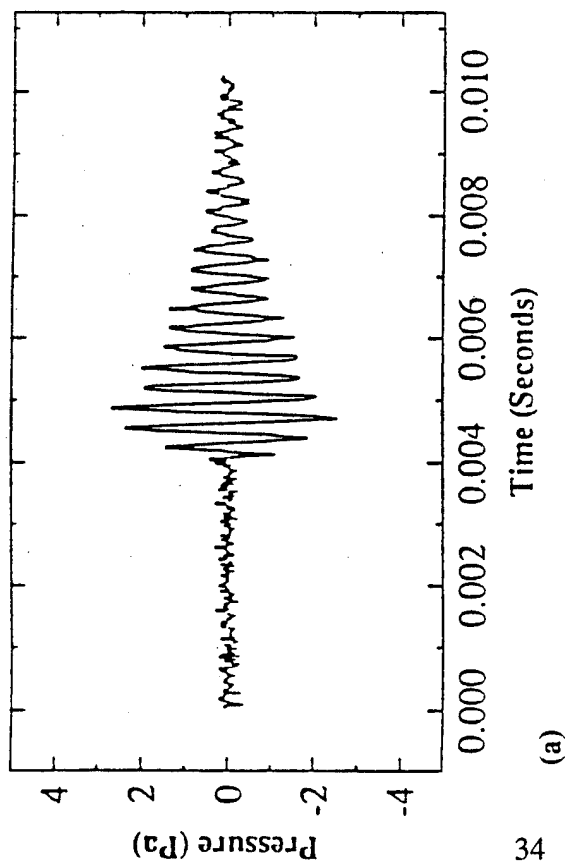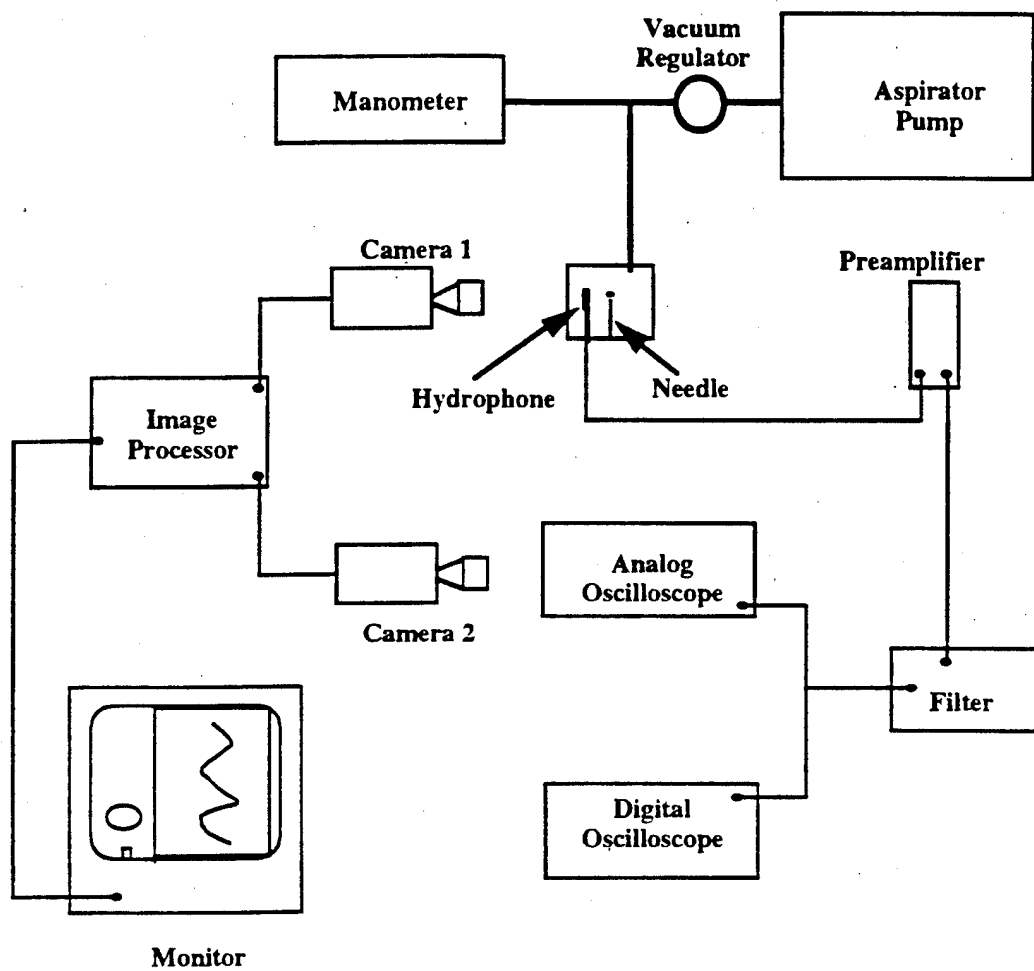
exponentially with the order n of the surface mode.

Fig. 1

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Fig. 2
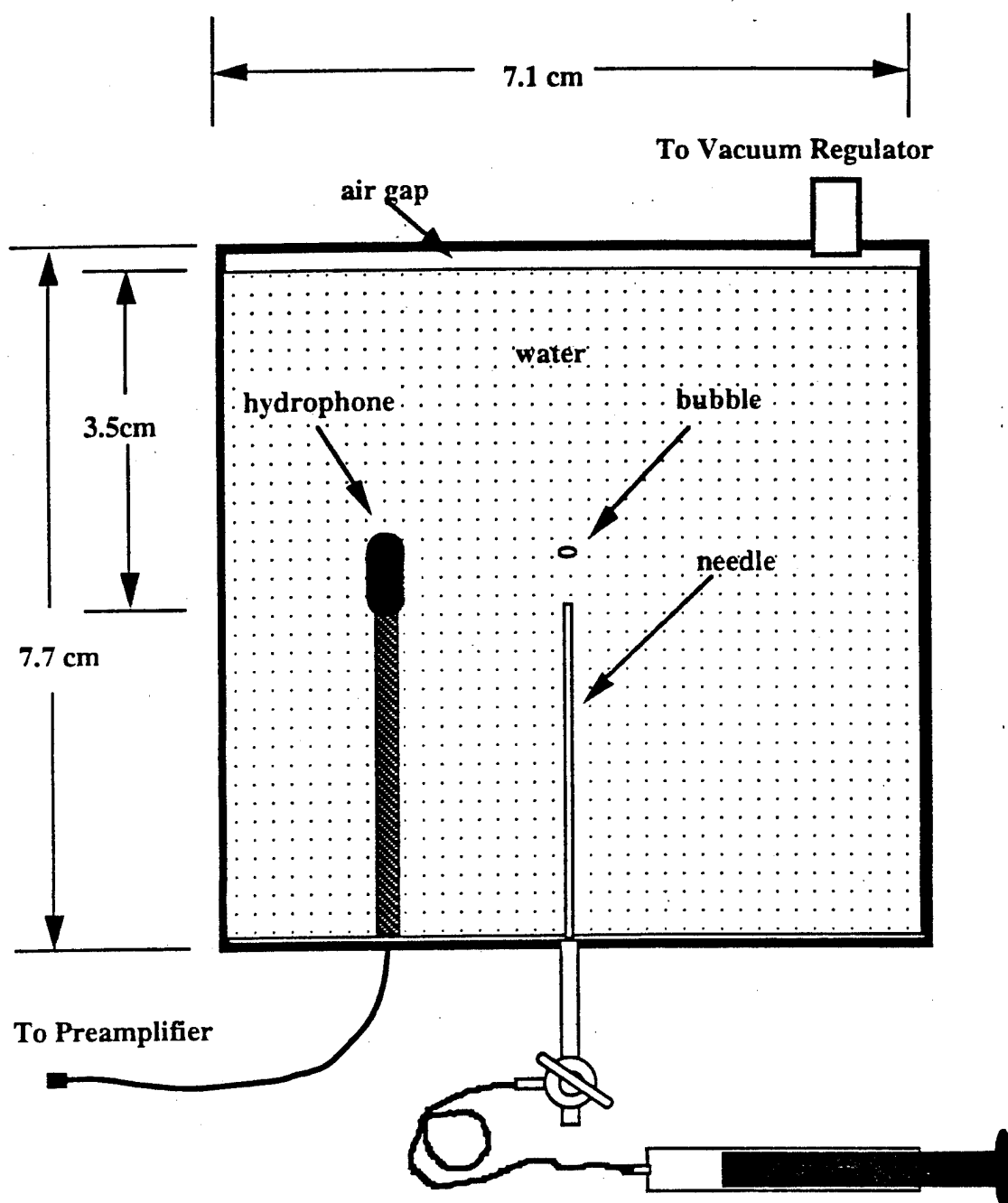
Fig. 3

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Fig. 5

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Fig. 7

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Fig. 8

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Fig. 9

Fig. 10

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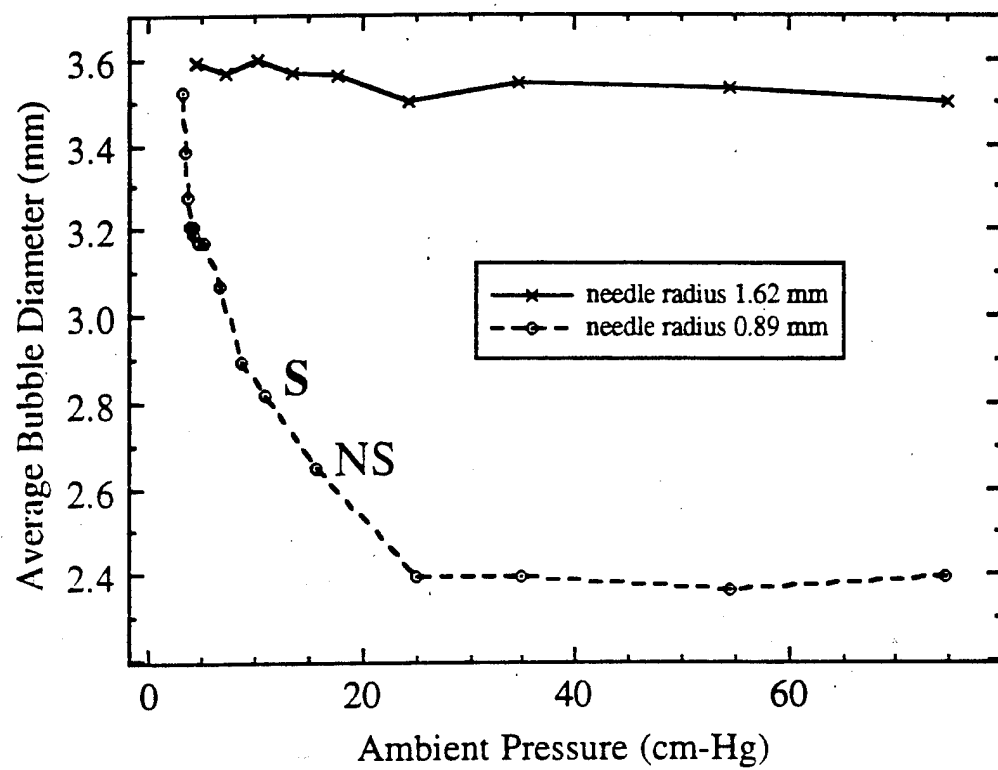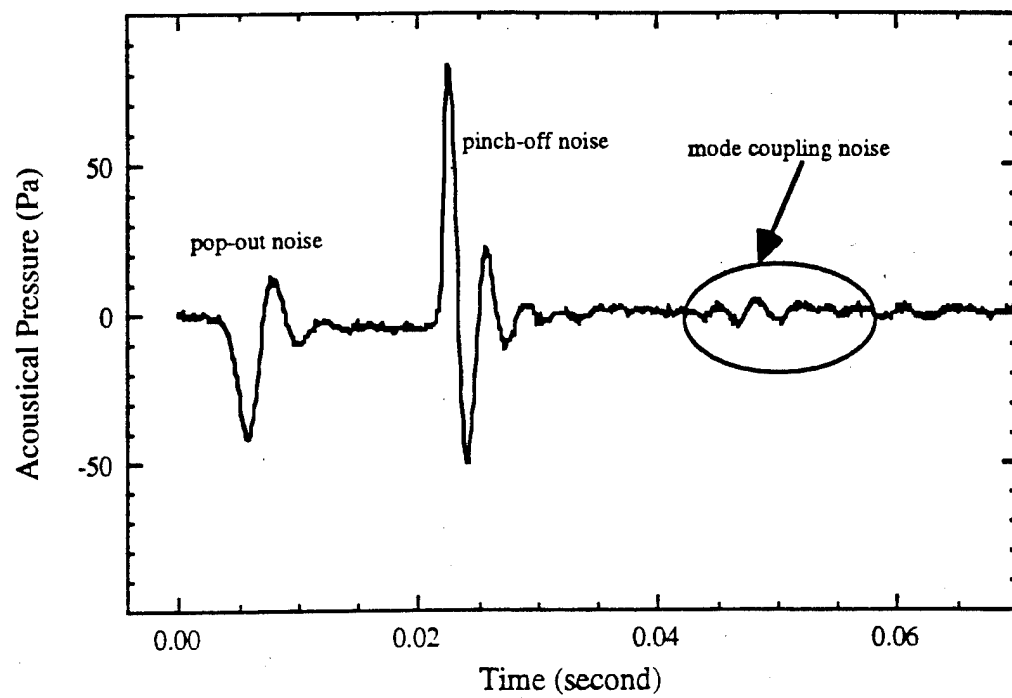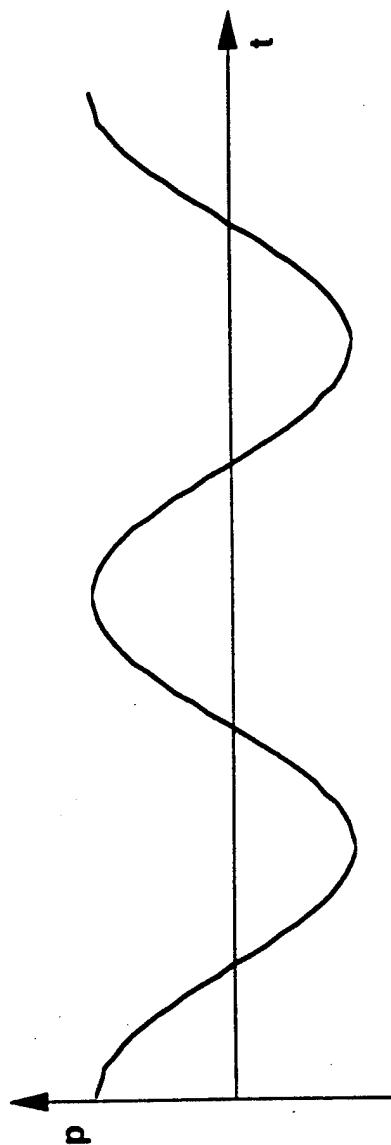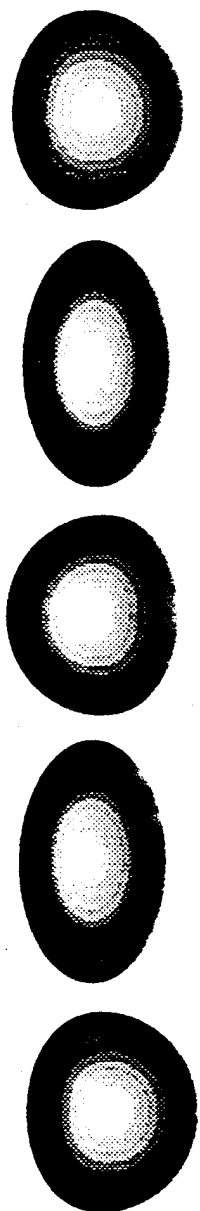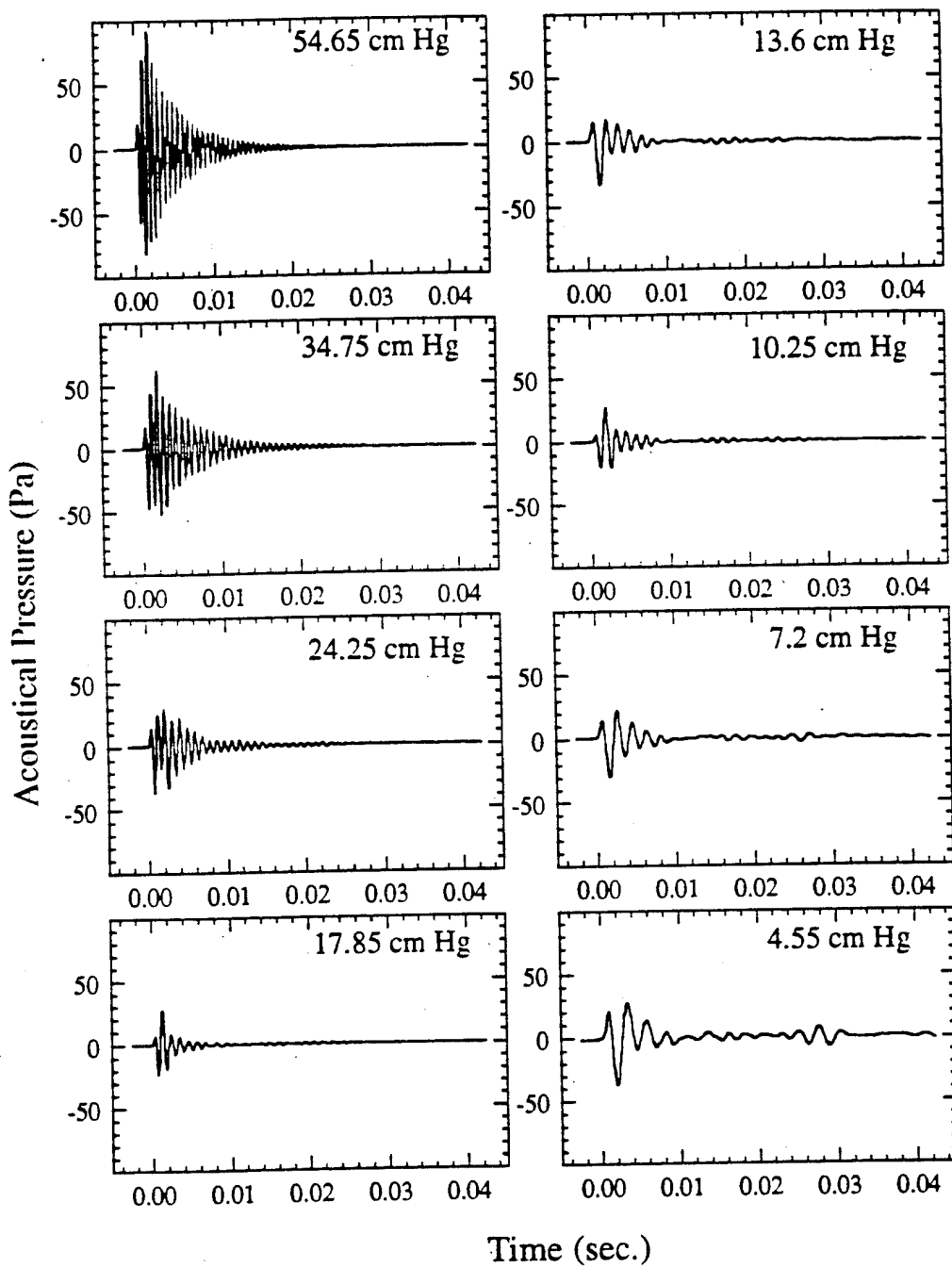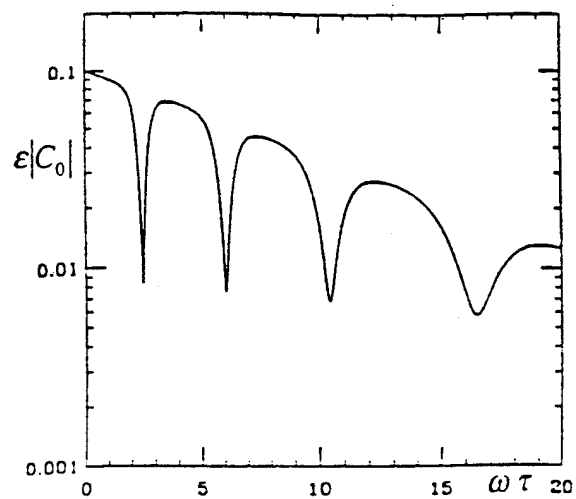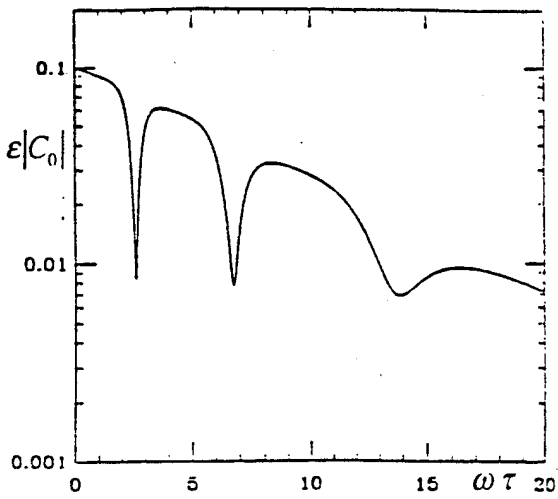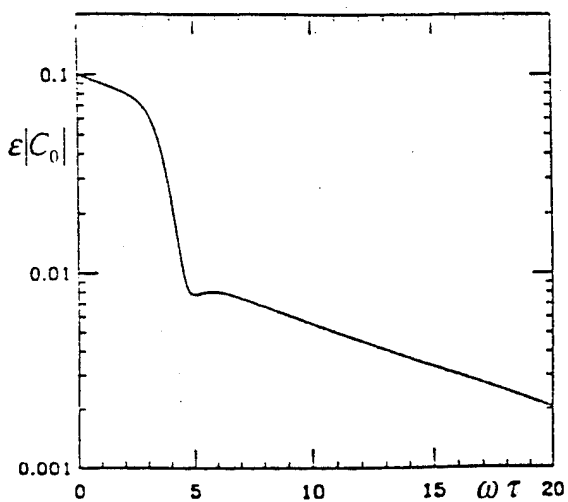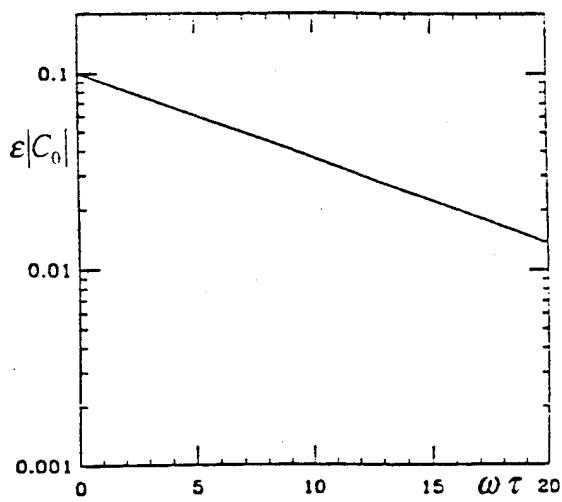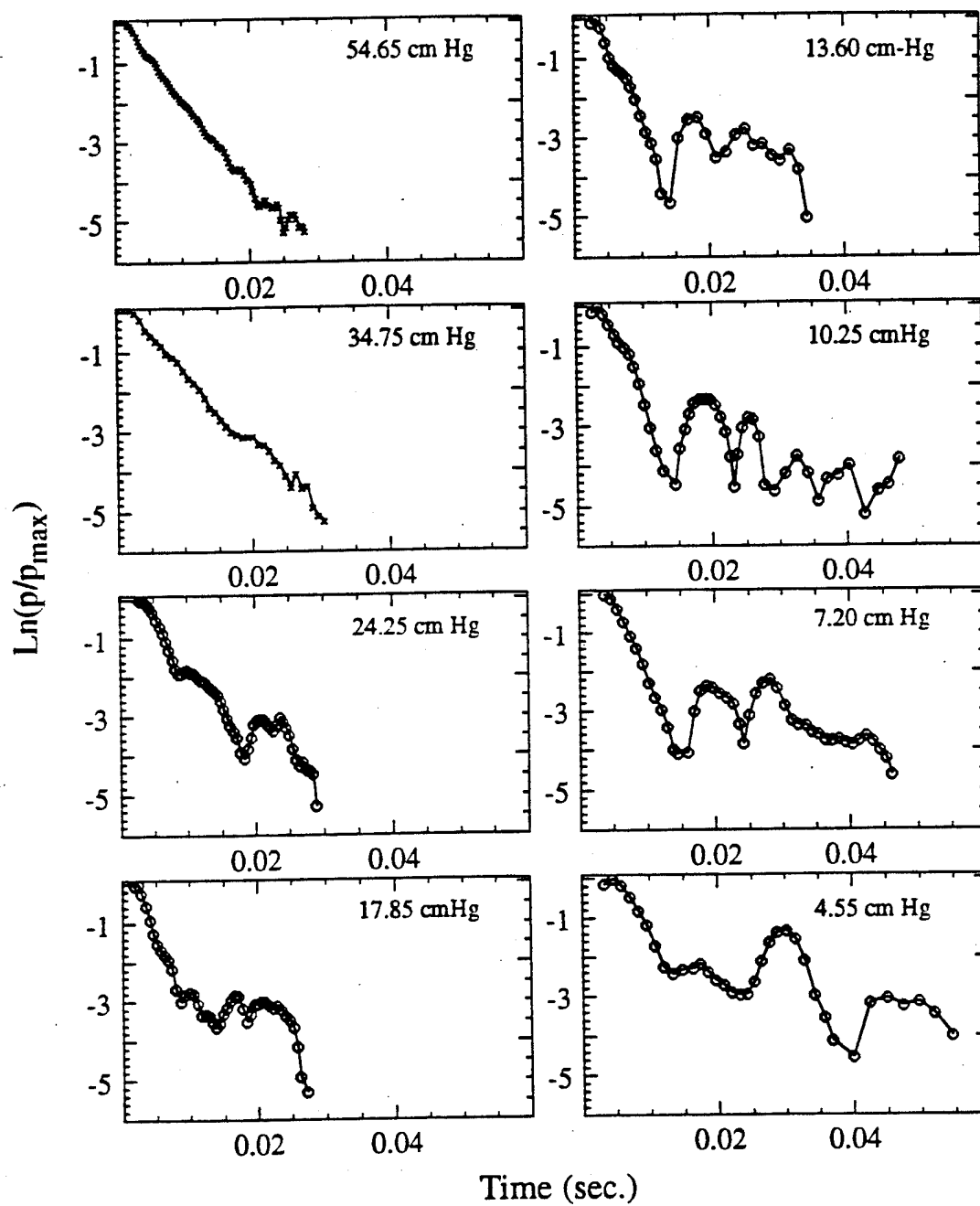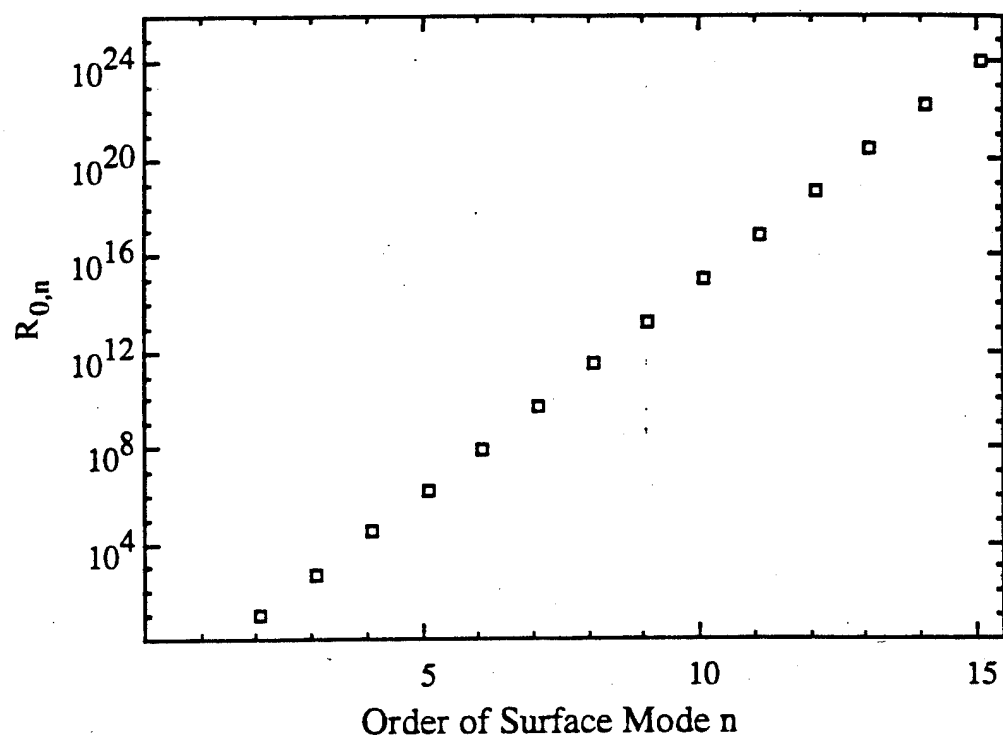
SONOLUMINESCENCE

A simple mechanical system can produce light from sound. In the process energy densities can increase by a factor of 10^{12}, and 50-picosecond light pulses are synchronized to a few parts in 10^{11}.

Lawrence A. Crum

And the four winds, that had long blown as one,
Shone in my ears the light of sound
Called in my eyes the sound of light.
— Dylan Thomas, "From Love's First Fever
to Her Plague"

In 1896 Henri Becquerel discovered that a uranium salt could darken a photographic plate, and from this effect he went on to discover radioactivity. In 1934 H. Frenzel and H. Schultes[1] exposed a photographic plate to acoustic waves generated in a water bath and also observed a darkening of the plate. They attributed that result to luminescence from the sound field—an effect that has come to be known as sonoluminescence. The luminescence they observed did not result from the sound field directly but arose through a process called cavitation, in which voids filled with gas and vapor are generated within the liquid during the tensile portion of the pressure variation. The subsequent collapse of these voids during the compression portion of the acoustic cycle can be extremely violent and represents a remarkable degree of energy concentration—as high as 12 orders of magnitude.[2] This energy concentration results principally from the fact that cavitation-bubble collapse obeys spherical symmetry, at least until the final stages, when instabilities in the interface may develop. This spherical symmetry is apparently preserved to submicron-size dimensions in single-bubble sonoluminescence,[3] resulting in another remarkable phenomenon: Extremely short bursts of light are emitted from the bubble with clock-like precision.

Multiple-bubble sonoluminescence

When the local acoustic pressure in the bulk of a liquid exceeds the threshold for cavitation, a zone develops in which many cavitation bubbles are activated. In a lab this cavitation is typically produced within an acoustic resonator or cell in which geometric focusing generates high acoustic-pressure amplitudes. (See figure 1.) If the cavitation is sufficiently intense, sonoluminescence occurs. In such "multiple-bubble sonoluminescence," many bub-

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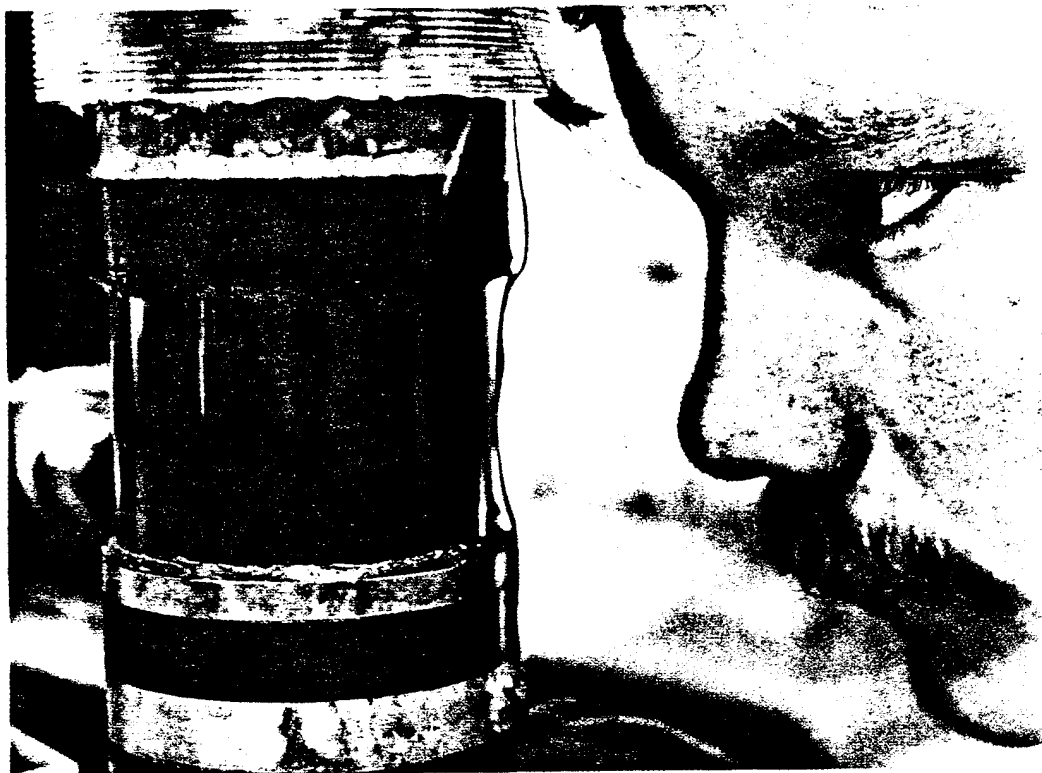
Acoustic cavitation and Sonoluminescence. This acoustic resonator consists of two transducers separated by a thin glass cylinder. Standing waves with frequencies from about 20 kHz to over 100 kHz and acoustic pressures up to about 3 bars can be generated in the liquid. If the acoustic-pressure amplitude is sufficiently large, many cavitation bubbles can be generated near the pressure antinodes of the standing-wave system. If the pressure is considerably lower, it is possible to "acoustically levitate" individual gas bubbles, which under conditions described in the text can generate light each acoustic cycle. Graduate student Sean Cordry watches the blue sonoluminescence from such a bubble. The red streak is an artifact of the lighting.
Figure 1

bles grow and collapse throughout the regions of most intense acoustic stress. Figure 2 shows typical MBSL, with a relatively large area of sonoluminescence activity containing many separate cavitation events, each emitting discrete bursts of light.

Sonoluminescence has been poorly understood because it is associated with the random growth and collapse of large numbers of cavitation bubbles. Moreover, the spatial scale of an individual event is on the order of a micron, and the temporal scale is on the order of a few nanoseconds. Thus, until recently, studies of sonoluminescence involved the time-averaged analysis of a cavitation field. Such a field contains many bubbles of various sizes, probably loosely coupled to each other in their dynamic behavior. These analyses were helpful in understanding gross aspects of the phenomenon, and proved useful in sonochemistry; however, because of the random nature of MBSL it was difficult to learn much about the physics of not only the individual cavitation events but also the resulting electromagnetic emissions.

Single-bubble sonoluminescence

This situation was substantially improved in 1988 when Felipe Gaitan,[3] after a painstaking search, discovered the conditions under which a single, stable cavitation bubble would produce sonoluminescence each acoustic cycle. The achievement of repetitive single-bubble sonoluminescence enabled this phenomenon to be examined in

considerable detail. That analysis has led to some remarkable discoveries.[4]

To attain SBSL, it is first necessary to drive a single bubble with an acoustic field intense enough to lead to relatively large radius excursions yet not so intense as to lead to self-destructive instabilities. The procedure Gaitan followed was to levitate a bubble in an acoustic standing wave. As the acoustic-pressure amplitude is slowly increased, a levitated gas bubble progresses through an evolution of states that can lead to SBSL; figure 3 diagrams this evolution. The "equilibrium radius" is obtained in the limit of no bubble oscillations. For relatively low pressures, the bubble undergoes low-amplitude radial pulsations and is positioned between the nodal and antinodal regions of the standing-wave field, where the buoyancy force is balanced by the acoustic radiation-pressure force. As the pressure amplitude is increased, the bubble moves closer to the antinode and eventually undergoes nonspherical pulsations (surface oscillations evidenced by a type of dancing motion of the bubble), which typically split the bubble into a number of small microbubbles. However, if the liquid is sufficiently degassed (say, to 10% of saturation), the dancing motion suddenly ceases. For an air bubble in pure water this happens at a pressure amplitude of about 1.1 bars. The bubble then becomes remarkably stable and emits a faint glow. This glow becomes brighter and brighter as the pressure amplitude is increased, eventually becoming
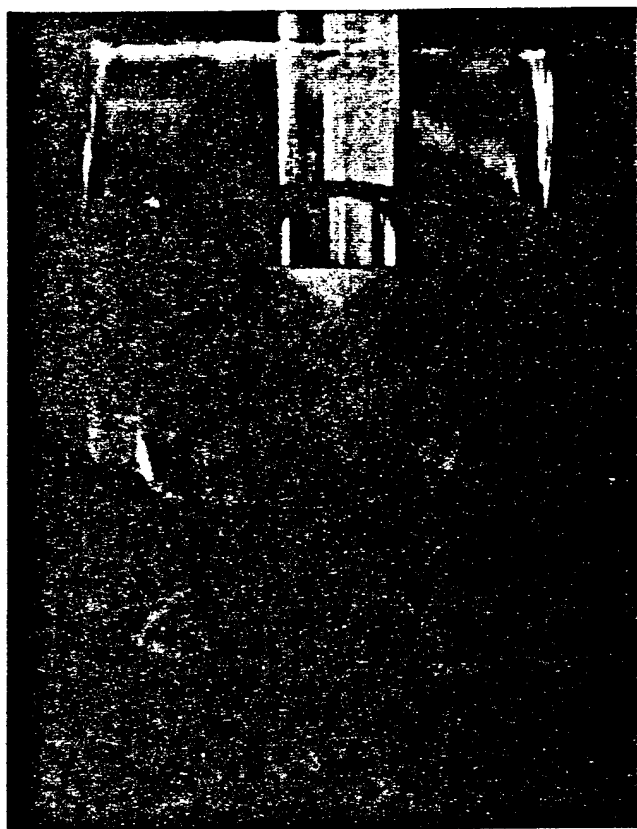
Multiple-bubble sonoluminescence produced by an ultrasonic horn at a frequency of 20 kHz. This is a double exposure: The thin, filamentary lines exist when the horn is driven at low acoustic intensity (2 W/cm²) and are associated with microscopic cavitation bubbles located near the antinodes of the standing-wave pattern. The bright, triangular-shaped area directly below the horn exists when the system is driven at a higher acoustic intensity (7 W/cm²); in this case there are no standing waves. For these photographs, Luminol was added to the water to produce more light in the visible region of the spectrum. Each exposure time was about 5 minutes at f/2.8. **Figure 2**

bright enough to be visible even with the lights on in the room. (See figure 1.) When the pressure is increased above about 1.5 bars, the brightly glowing bubble suddenly disappears.
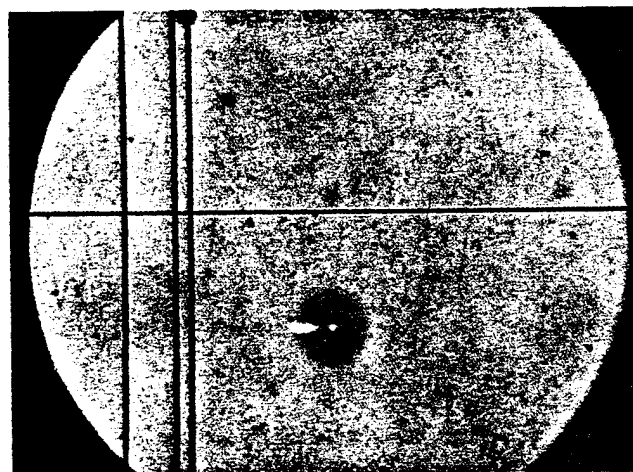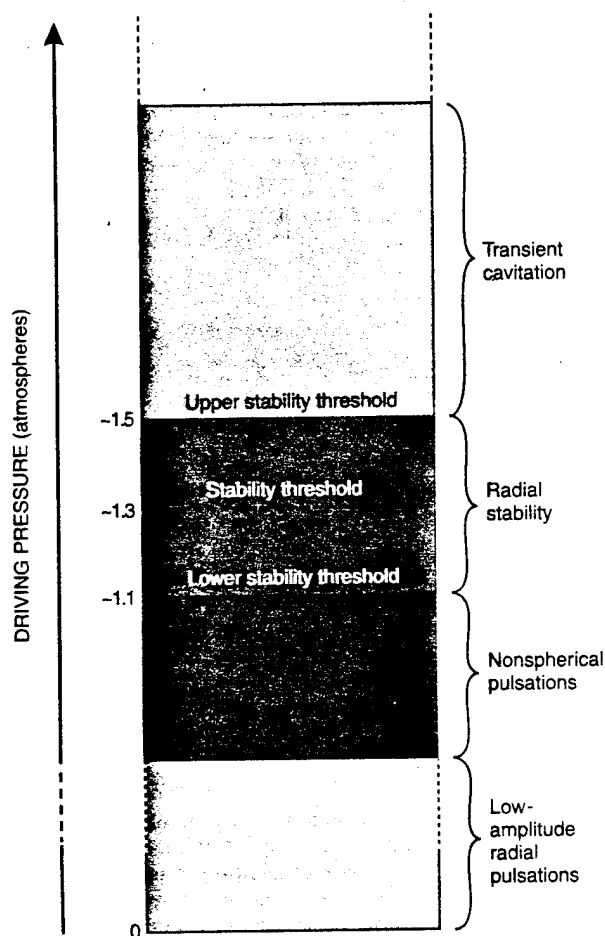
It is likely that diffusion of gas through the liquid–bubble interface plays an important role in bubble stability and restricts the conditions under which SBSL can occur.[5-7] Consider an oscillating bubble in a liquid that contains dissolved gas. When the bubble is in its expansion phase, gas will diffuse into the bubble; conversely, when it is in its compression phase, gas will diffuse out of the bubble. For small-scale oscillations and linear excursions of the bubble radius, the total acoustically induced mass flux of gas over one complete cycle will be zero, and the bubble will dissolve slowly as a consequence of surface tension. However, for larger oscillations (at higher acoustic-pressure amplitudes) there is considerable temporal asymmetry in these radius excursions: The time that the bubble spends in its expansion phase is large compared with the time it spends in its compression phase. Thus over a complete cycle, more gas will diffuse into the bubble than will diffuse out, and the bubble will grow.

This "rectified diffusion" is reduced if the amount of gas dissolved in the liquid is less than the saturation level. Consequently, if the liquid is considerably undersaturated with gas, stable bubble size can be achieved only for large displacement amplitudes. Of course, a balance of diffusion should occur only for a unique pair of values of the dissolved gas concentration and the driving pressure amplitude—which implies that the equilibrium is unstable. However, apparently because of nonlinearities in the bubble response, stable equilibrium conditions can occur.[5-7] Hence greatly reducing the dissolved gas concentration makes it possible to produce a single, stable cavitation bubble that undergoes large radius excursions each cycle. Gaitan was able to find the conditions necessary for these radial excursions to produce sonoluminescence in each

oscillation. Once those conditions are achieved the system is amazingly robust: Unless there are significant changes in the acoustic or liquid parameters, SBSL can be maintained for unlimited periods of time.

One can determine the conditions for the bubble dynamics that lead to SBSL rather straightforwardly with light-scattering techniques.[3,8] Using a laser, a photodetector and the applicable Mie-scattering algorithms, one can invert the scattered intensity and obtain a radius-versus-time curve for the bubble. One finds that the light emissions occur on bubble collapse and that the phase of those emissions stays rigorously fixed over a number of acoustic cycles. (See figure 4.)

A group headed by Seth Putterman at the University of California, Los Angeles, has used the constant-phase result and a much improved light-scattering technique to obtain radius–time curves for SBSL to a high level of precision.[8,9] These curves, shown in figure 5, illustrate the transition from a nonsonoluminescing bubble to a sonoluminescing one and are very useful for understanding critical aspects of this phenomenon. As the acoustic-pressure amplitude is increased, there is a transition point at which the bubble's equilibrium radius (apparent at early and late times in figure 5), its maximum radius and its rebound from implosive collapse are all suddenly reduced. At this pressure sonoluminescence emissions begin to occur. Computations of these radius–time curves using standard models of nonlinear bubble dynamics predict the rebound reduction at the reduced bubble size; however, the sudden decrease in equilibrium radius is still not clearly understood. It is known that in most cases surface waves exist on the bubble just prior to the onset of sonoluminescence. However, when sonoluminescence conditions are met, the bubble becomes amazingly stable and shows no evidence of shape instabilities. The parameter space for SBSL occurrence is a topic of current interest. To date, no liquids other than water and

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DRIVING PRESSURE (atmospheres)

~1.5
~1.3
~1.1
0

Upper stability threshold
Stability threshold
Lower stability threshold

Transient cavitation
Radial stability
Nonspherical pulsations
Low-amplitude radial pulsations

Pressure regimes of single-bubble sonoluminescence. The behavior of an acoustically levitated bubble in an aqueous liquid changes with acoustic driving pressure, as shown schematically at left and described in the text. A photograph of SBSL (above) shows light emissions from a single, stable cavitation bubble that is oscillating about an equilibrium radius of a few microns and emitting blue light each acoustic cycle. The sonoluminescence appears to be coming from the very center of the bubble. The diffuse background light shows that the maximum radius of the bubble is on the order of 50 microns (the outer fiducial lines are 105 μm apart). Over this 1-second exposure, the bubble underwent about 20 000 complete cycles. The horizontal white line is reflected light from an illuminator aimed directly at the bubble. **Figure 3**

glycerin–water mixtures have been shown to demonstrate this phenomenon, although there is no a priori reason why it shouldn't exist in many liquids.

Putterman and his colleagues have examined SBSL in some detail and have discovered some of its remarkable properties.[2,6,8–11] One particularly interesting discovery arose from their attempts to measure the pulse duration of the sonoluminescence flash. They found that as they selected photomultiplier tubes with increasingly faster response times, they continued to measure only the impulse response of the tubes. Even when they used the world's fastest microchannel-plate photomultiplier tube they were unable to obtain a direct measurement of the SBSL pulse duration.[2] Furthermore, when they compared the impulse response of the SBSL flash with that of a 34-picosecond pulsed laser, they determined that the SBSL flash is extinguished faster than that of the laser, probably due to some residual ringing in the laser that is absent in SBSL. Attempts to measure the pulse duration with streak cameras and other high-speed devices have been unsuccessful. Although a precise value for the pulse duration has not yet been obtained, Putterman's group estimates an upper bound of 50 psec (see PHYSICS TODAY, November 1991, page 17). This extremely short time (as compared with the acoustic period of about 40 microseconds) is difficult to explain in terms of our conventional understanding of bubble dynamics.

A second remarkable aspect of SBSL is the degree of synchronicity of the flashes. If the relative phase angle between the zero-point crossing of the acoustic field and the emission of the sonoluminescence burst is measured, it is found to be stable to within a degree for periods of several minutes.[3] When the pulse-to-pulse jitter was

measured,[9] the standard deviation of the Gaussian curve that defines the jitter was on the order of 50 psec. This remarkable clock-like synchronicity is amazing when one considers that the jitter in the synchronous output of the frequency synthesizer used in the experiment was on the order of 3 nanoseconds. Phase-locking of the flashes is no longer guaranteed, however, if the levitation vessel is driven slightly off resonance.[12] In fact, for that case analysis of successive intervals between flashes shows period-doubling, quasiperiodic and even chaotic behavior.

Sonoluminescence spectra

Because sonoluminescence is indicative of the high temperatures and pressures generated by cavitation collapse, measuring the spectrum of this light has been of interest for many years. Figure 6 shows some representative spectra. In the spectrum of MBSL generated within an organic liquid such as dodecane, one sees well-defined spectral bands that are characteristic of the host liquid. For example, the well-defined peaks in the dodecane spectrum shown in figure 6 are associated with diatomic carbon. By generating synthetic spectra that closely approximate the measured spectra, Kenneth Suslick and his colleagues[13] have obtained the "effective temperature" of the constituents that give rise to the sonoluminescence. This technique depends upon the ability to resolve recognizable emission bands generated by atomic and molecular transitions. Indeed, in hydrocarbon solutions containing dissolved metallic compounds or salts, one sees discrete metal line emissions. When the spectrum of dodecane was measured, with argon as the dissolved gas, the synthetic spectrum indicated that the effective temperature of the C_2 excited state was 5100 K. These measurements
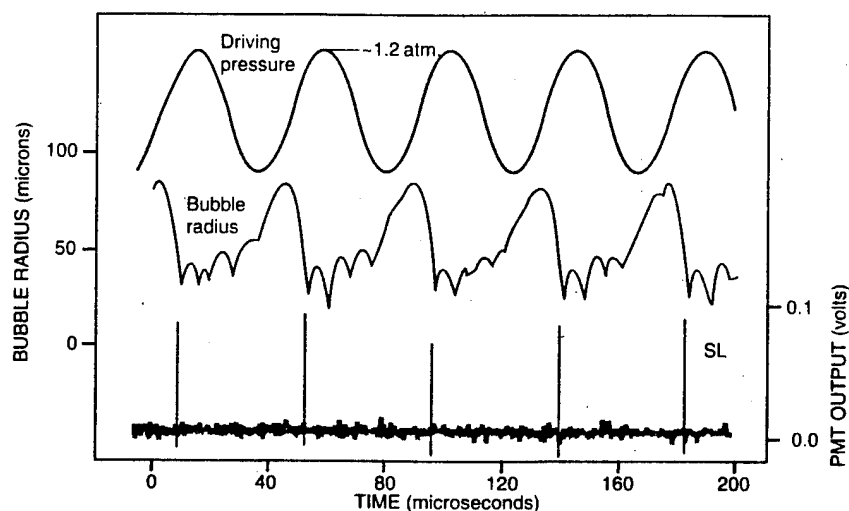
Synchronous relationship between the acoustic field (top), the measured radius-versus-time curve (middle) and the SBSL emissions measured with a photomultiplier tube (PMT) (bottom). The emissions occur at a fixed phase of the acoustic field. (Adapted from ref. 3.) **Figure 4**

were all performed under conditions of MBSL, as in figure 2. In this case bubble–bubble interactions are likely to occur.

Figure 6 also shows the spectrum of water generated under MBSL conditions.[14] This spectrum is considerably different from that of dodecane and shows a well-defined peak at 310 nm. This peak can be associated with molecular bands of the OH free radical, which is likely to be produced by the high temperatures and pressures within the bubble.

Extensive spectroscopic measurements of SBSL in water have also been undertaken[11] and show some intriguing results. For example, the SBSL spectrum is remarkably smooth, containing no significant peaks, and can be fit quite closely by a blackbody curve—giving an effective temperature as high as 30 000 K under some conditions. Furthermore, the sonoluminescence intensity of a pure nitrogen bubble is only a few percent of that of an air bubble, but with the addition of only 1% argon (its approximate abundance in air), the sonoluminescence intensity returns to that for air. With a pure xenon gas bubble, a broad maximum in the spectrum is observed near 300 nm. No such maximum is observed for a pure helium bubble. For both pure Ar and He the intensity increases with decreasing wavelength until the ultraviolet cutoff for water is reached. These results suggest that complicated physical chemistry is occurring within the sonoluminescing bubble.

A typical spectrum of SBSL in water, obtained by Anthony Atchley and his colleagues,[15] is shown in figure 6. When one compares this spectrum with that of MBSL in water, one sees that the 310-nm peak is barely visible and that the spectrum now extends deeply into the ultraviolet. In fact, there is still uncertainty about whether the peak at about 230 nm in the SBSL spectrum is real or is simply the result of the uv attenuation within the water and the measurement apparatus.

The SBSL spectrum doesn't appear to have any spectral bands or emission lines indicative of well-known atomic and molecular transitions and thus doesn't lend itself to a comparison with synthetic spectra. (Perhaps the bands are there but are so broadened by the high temperatures and pressures that they aren't recognizable.) It may be that the spectrum is more closely approximated by that of a blackbody and that the temperature of sonoluminescence is relatively high. The blackbody fit[15] of the SBSL spectrum in figure 6 indicates an effective temperature of approximately 16 000 K. When one lowers the temperature of the water, the SBSL spectrum shifts toward shorter wavelengths; indications of temperatures as high as 30 000 K are then found, provided the blackbody assumption is made.[11] This issue of the temperature of sonoluminescence is still unresolved. Of course, whether one can even have a "temperature" (which implies some sort of equilibrium) of 30 000 K for 50 psec is debatable.

Some basic theory

The theoretical analysis of acoustic cavitation and bubble dynamics in general is reasonably mature,[16] having been initiated, in some sense, by Lord Rayleigh. While MBSL is complicated by the presence of many bubbles, SBSL, in which a single bubble is driven into spherical pulsations at a relatively low driving pressure, seems to represent an idealized case that would be adequately described by existing theoretical models. Hence the discovery of SBSL has provided an exceptional opportunity to test existing theories of bubble dynamics.

Because the gas bubble is an inherently nonlinear system, the theoretical treatment of cavitation-bubble dynamics is necessarily complicated and is best approached through numerical methods. These analytical–numerical approaches usually involve an equation of motion for the bubble interface, an energy equation for both the liquid and the gas, and the application of momentum conservation across the gas–liquid interface. These coupled nonlinear differential equations are then solved, using an equation of state for the gas in the interior of the bubble. The solution describes the motion of the interface and allows one to infer values for the internal pressure and temperature.[5,16] Using such an approach, Bradley Barber and Putterman[8] obtained excellent agreement with their measured radius–time curves. (To be sure, because neither the equilibrium radius of the bubble nor the acoustic-pressure amplitude at the site of the bubble can be measured precisely, these variables were treated as adjustable parameters.) Thus it seemed reasonable to assume that the temperature and the sonoluminescence pulse duration also ought to be describable with this theoretical analysis.

Unfortunately, there is a major failure in the analysis. Figure 7 shows the predicted behavior of the radius and temperature as a function of time for typical conditions that give rise to SBSL: an acoustic-pressure amplitude of 1.3 bars, an equilibrium bubble radius of 5 microns and a driving frequency of 25 kHz. The initial 5-micron bubble radius expands to nearly 40 microns and then rapidly collapses to a value on the order of 0.1 micron. The temperature within the bubble is predicted to rise to

values on the order of 7000 K. These numbers are in reasonable agreement with the measured or inferred values; the predicted duration of the sonoluminescence pulse is not. It can be seen from the expanded portion of the graph that the temperature is expected to exceed 2000 K for about 20 nsec. By contrast, it would be impossible to draw a line on this figure that would accurately represent the upper bound on the measured pulse duration of 50 psec! How can the contents of the bubble remain compressed for such a long period of time and not radiate?

Imploding shock waves

There are a variety of competing hypotheses that attempt to explain the observed behavior of both SBSL and MBSL. A particularly intriguing interpretation, proposed by the late Julian Schwinger,[17] is based on the dynamic Casimir effect. So far, this mechanism exists principally in mathematical form and has not been tested against experiments. A second hypothesis involves an electrical discharge mode in which asymmetric bubble collapse brings about charge separation.[18] This hypothesis can explain several observed phenomena of both SBSL and MBSL, but the model involves complicated bubble dynamics that do not reproduce the high level of synchronicity observed in SBSL.

It was suggested more than 20 years ago that MBSL originates from a shock wave in the gas contained within the bubble rather than from the adiabatic heating of the gas.[14] This concept has received renewed interest with the recent discovery of the extremely short duration of the SBSL flash. Theoretical studies of the generation of an imploding shock wave within the gas that gives rise to SBSL emissions give results consistent with much of

the experimental data.[19,20] For example, the measured luminosity of the SBSL emissions for an air bubble in water is on the order of 30 mW. The luminosity calculated[19] on the assumption that the emissions are thermal bremsstrahlung is on the order of 100 mW. The velocity of the imploding shock wave has also been calculated; by finding the distance from the center at which the gas is heated to luminescence temperatures, the researchers obtained a pulse duration on the order of tens of picoseconds,[21] in good agreement with experiment. However, they provided no information on the shock rebound, and whether or not this model would lead to the observed rapid extinction of the SBSL emissions remains unclear.

The strong probability that SBSL results from an imploding shock wave has now made this curious phenomenon one of considerable interest. Because the bubble is relatively far removed from the symmetry-breaking container boundaries, is driven at a relatively low acoustic pressure and is small enough that surface tension tends to force it to remain spherical, the imploding shock wave very likely remains symmetrical until the final stages of collapse. This spherically symmetric implosion has the potential for creating some exotic physics and chemistry. Calculations suggest that temperatures as high as 10^8 K are to be expected.[19] This result has in turn prompted calculations of the possibilities of inertial confinement fusion with a deuterium–tritium gas mixture, which yield a qualified estimate of 40 neutrons per second under ideal conditions.[9] While the possibilities of actual fusion in this system are remote, the likelihood that the gas in the bubble remains relatively cold until the final stages of collapse suggests that one could use this simple and
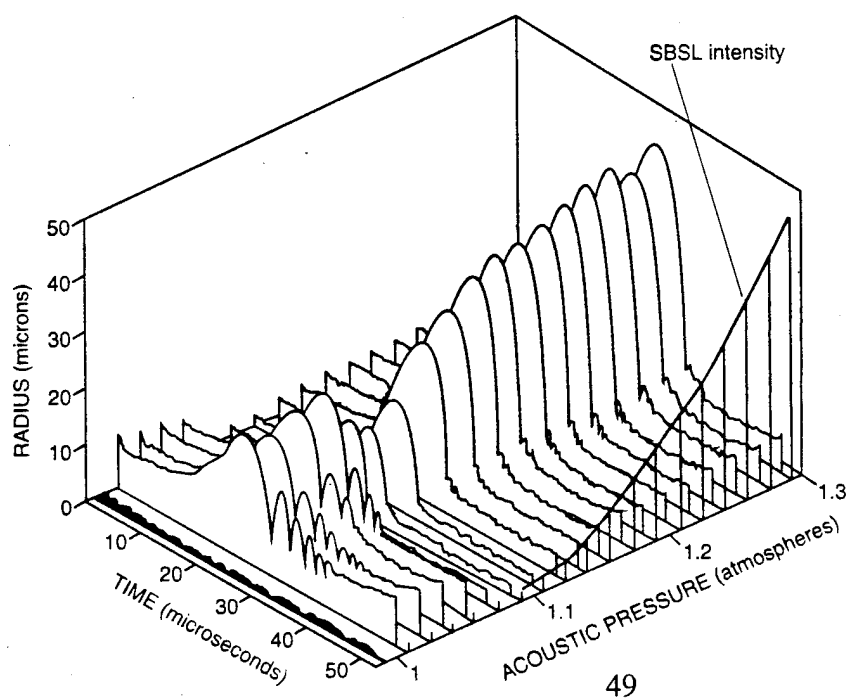
Conditions for SBSL. These light-scattering measurements illustrate the change in the behavior of the radius–time curve when sonoluminescence conditions are achieved. The unshaded regions are for a nonsonoluminescing bubble; the blue-shaded regions are for a sonoluminescing bubble. For pressures insufficient for sonoluminescence, there are significant rebounds in the bubble radius. After sonoluminescence is achieved, the rebounds are nearly absent. Note also the sudden shift in the equilibrium radius (apparent at early and late times) to smaller values when sonoluminescence conditions are met. As the pressure is increased above about 1.3 bars, the bubble suddenly disappears. (Adapted from ref. 9.) **Figure 5**
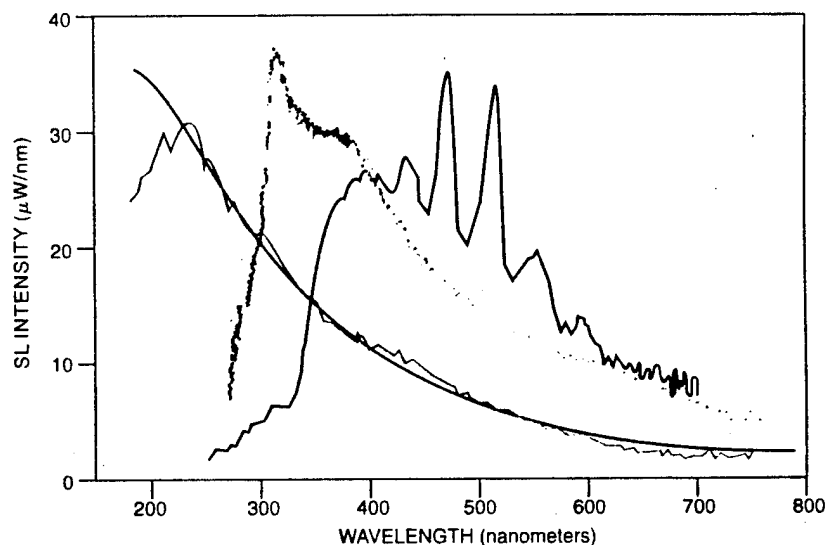
Sonoluminescence spectra. The red curve is for MBSL in dodecane.[13] The blue dots are for MBSL in water at a frequency of 16 kHz and a temperature of 25 °C.[11] The green curve is for SBSL, also in 25 °C water, driven at 43 kHz;[15] the smooth curve is the tail of a blackbody curve for a temperature of 16 200 K (the maximum is off the scale). The scale on the left applies only to the green curve; the scales for the other two curves have been arbitrarily shifted for comparison purposes. **Figure 6**

inexpensive system to obtain information about inertial confinement fusion. In both cases, the stability of the imploding shock wave limits the ability to concentrate energy.

The imploding-shock-wave hypothesis has been critically examined only in SBSL, because this simple system lends itself much more readily to experimentation. The acoustic-pressure amplitude that drives the bubble in SBSL is quite low by cavitation standards—on the order of 1 bar—and a barely discernible shock wave is generated within the liquid.[7]

If the microscopic inhomogeneities that serve as cavitation nuclei for MBSL are removed from the water, dynamic tensile strengths as high as 250 bars can be momentarily achieved. Then when cavitation does occur (nucleated by an adventitious cosmic ray, for example), the "event" typically lasts for only a few acoustic cycles (it quickly destroys itself) and can be extremely violent. For example, at this level of acoustic pressure the shock waves generated within the liquid as a result of bubble collapse are occasionally so intense that they can even destroy the resonator that produces the acoustic field. Such shock waves are often credited with the destructive effects of cavitation, such as the erosion of metal surfaces. If imploding shock waves exist within cavitation bubbles driven at these very large pressure amplitudes, then temperatures and pressures should be expected that greatly exceed those achieved in SBSL. Of course, if the shock wave is not launched before the inevitable instabilities in the air–liquid surface develop, then a focused shock-wave implosion in the gas probably will not occur and the contents will be heated by an adiabatic compression of the bubble itself. Thus one should expect MBSL-type behavior in that case. However, it seems likely that in at least a few of these events internal shock waves would occur that would be similar to those postulated for SBSL but driven at much higher initial velocities. Because of the transient nature of the phenomenon it would be very difficult to determine if and when these "super

shocks" occurred. Perhaps by-products of such cataclysmic events could be detected.

Applications and future perspectives

The amazing robustness of SBSL suggests that there may be technological applications in a variety of disciplines. Consider the measurements of the synchronicity of this phenomenon, which demonstrated that the stability of the system is on the order of 5 parts in 10^{11}. Those measurements were made without knowledge of the origin of this stability and there were no serious efforts to improve it. That suggests that it might be possible to develop a cheap precision frequency source based on SBSL.

Although sonoluminescence is intriguing in and of itself, this phenomenon is primarily a diagnostic indicator of the enormous energy concentration that can arise from the implosive collapse of a cavitation bubble. The technological use of this energy concentration has great promise. For example, there is considerable potential for influencing chemical reactions in an extended region of violent cavitation activity, as in the MBSL shown in figure 2. Research in the relatively new discipline of sonochemistry suggests that many chemical reactions can be influenced by ultrasound—a technology whose potential for industrial applications is gradually being recognized. To take one example, the conventional reactor process for reducing potassium iodide to iodine takes hours; when ultrasound is used at a frequency of 20 kHz the reaction time is reduced to a few minutes; when a combination of the frequencies of 20 kHz and 1 MHz is used the reaction time is reduced to milliseconds. Industrial-sized reactors that take advantage of these gains are being developed for commercial use.[22]

Sonochemistry takes advantage of the unique characteristics of acoustic cavitation to concentrate mechanical energy onto microscopic scales. When a cavitation bubble collapses, the resulting high temperatures most likely last on the order of nanoseconds or less. In standard chemical procedures a short-lived, newly created high-temperature
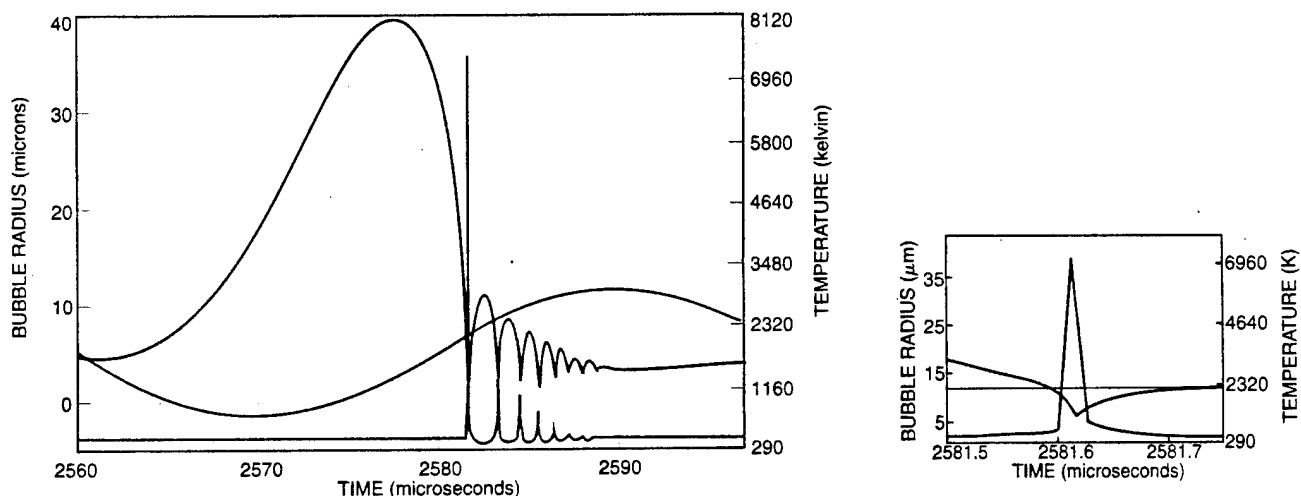
Expected behavior of the bubble radius and internal temperature during SBSL. The purple curve is the acoustic pressure with a driving frequency of 25 kHz. The pressure amplitude is 1.3 bars. The red curve is the bubble radius after the transients have died down (about 60 cycles into the oscillations). Temperature is shown by the green curve. On the right is an expansion of the data around the bubble collapse region. Theory predicts that the temperature of the contents of the bubble should be about 2000 K for over 20 nsec; however, the measured sonoluminescence pulse duration is only 50 psec—a time so short that it can't be drawn to scale on the figure. (Results courtesy of Vinod Kamath.) **Figure 7**

species will revert back to its initial constituents before the high temperatures can be reduced. In acoustic cavitation, on the other hand, the rapid quenching of the reaction "freezes out" the new species. Consider the production of amorphous (noncrystallized) iron, a product of considerable commercial interest for its catalytic capabilities. It is difficult to cool a liquid metal rapidly enough to prevent crystallization. However, in the chemical reactor within a cavitation bubble, ferrous compounds can be decomposed into free atoms and then quenched on such short time scales that solidification of the iron can occur before crystallization.[23] Amorphous iron is easily produced on a laboratory scale by this technique.

To date, SBSL has been demonstrated only in water and mixtures of glycerin and water. It is known from MBSL studies that the intensity of sonoluminescence scales with σ^2/p_v, where σ is the surface tension and p_v is the vapor pressure.[24] MBSL is known to occur in liquid metals such as mercury. If SBSL could be demonstrated in mercury, and the σ^2/p_v scaling parameter holds, then one should expect sonoluminescence intensities nearly 10 000 times greater than what one finds for water.

Energy concentrations of 10^{11}, temperatures of 30 000 K, optical pulse synchronicities to a few parts in 10^{11}, pulse durations of 50 psec, production of exotic chemical species and imploding shock waves—all this from a simple mechanical system costing a few hundred dollars to construct! Although the phenomenon of light from sound has been known for 60 years, the recent discovery of single-bubble sonoluminescence has enabled us to access a remarkable laboratory for physics and chemistry.

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Sonoluminescence

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Sonoluminescence

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When trapped in sufficiently intense acoustic fields, single bubbles of gas can emit luminescence bright enough to be visible in an undarkened room. The large number of intriguing results recently published about such single-bubble sonoluminescence (SBSL) [1–9] suggests that this phenomenon awaits a full explanation. And as reported by Hiller et al. on page 248 of this issue [10], some exciting atomic physics may be occurring within the collapsing cavitation bubble that gives rise to SBSL. However, many of the results they present are also anomalous and defy immediate explanation.

Sonoluminescence (SL) was discovered nearly 60 years ago when Frenzel and Schultes [11] found that photographic plates became exposed when submerged in water and irradiated with ultrasonic waves. Since then, the phenomenon of SL has been associated with the presence of (relatively) intense sound fields within liquids. The light emission implies existence of high local temperatures (the ambient temperature of the liquid remains relatively constant), temperatures high enough to incandesce gas and influence chemical reactions. Thus arose sonochemistry, which has resulted in an active field of both basic research and emerging technology development [12].

When an intense sound field is produced within a liquid, microscopic cavities of gas or vapor can be generated when the liquid fails under tensile stress. The subsequent acoustic compression cycle forces these cavities to collapse violently, which results in a remarkable concentration of mechanical energy, estimated to be as high as 12 orders of magnitude [3, 4, 10]. In the process, the gas contained within these cavities is heated to luminescence. In some cases, the light emissions appear to come from a distributed region surrounding the tip of the acoustic source. This multiple-bubble sonoluminescence (MBSL) results from the collapse of many separate, individual cavitation bubbles. Because MBSL occurs randomly and transiently, it has been difficult

to study in much detail. Recently, Gaitan and co-workers discovered the unique conditions necessary for a single bubble, pulsating stably, to emit SBSL each acoustic cycle [1, 2] (see figure); its robust stability and simplicity has permitted detailed studies of this "hydrogen atom of sonoluminescence" [1, 4, 10].

Theoretical calculations of the time interval during which the contents of a gas bubble, driven to collapse by the sound field, is sufficiently heated to emit light tend to be on the order of tens of nanoseconds. However, when Barber and Putterman sought to measure the duration of the light flash, they discovered that they were in fact measuring the impulse response of their photomultiplier tube (PMT) [3]. Even subsequent measurements obtained with the world's fastest multichannel plate PMT led to results that were rise time limited. Their best measurements to date indicate an upper bound of about 50 ps, about 1/1000 of

that predicted by conventional theory of cavitation bubble collapse. In addition, Barber and Putterman measured the statistics of the flash-to-flash interval for a bubble driven at 30 kHz and discovered that it had an average value of 33 µs with a root mean square fluctuation of only 50 ps [3]. This remarkable stability, 1 part in 10^6, exceeds the rated stability of the frequency generator that drove the acoustic system.

The spectrum of MBSL contains molecular emission bands associated with the liquid in which the sonoluminescence occurs [12]. For example, if MBSL occurs in an organic liquid such as dodecane, one sees diatomic carbon bands; if MBSL occurs in an inorganic liquid such as water, one observes the spectral bands of the OH radical; these bands suggested temperatures within the
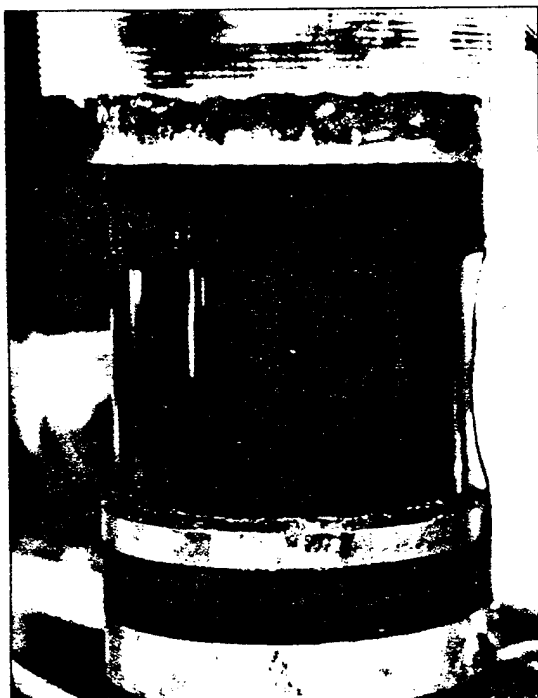
Bright bubbles. An acoustic standing wave levitates a small gas bubble near the center of a glass cell **(left)** and drives that bubble to radial excursions of sufficient amplitude to generate sonoluminescence each and every acoustic cycle. Note the bright spot at the center of the cell, which can easily be seen without darkening the room; no chemical enhancement is required. This bubble was driven at a frequency of 22.3 kHz and at a pressure amplitude of about 1.3 bar. In an example of MBSL **(right)**, the intense sound field near the tip of an acoustic source produces many transient cavitation bubbles that grow and collapse with such violence that they heat their respective interiors to incandescence. Because the individual bubbles persist for only a few acoustic cycles (at 22 kHz), they are not visible in this photograph. Luminol, a wavelength shifter, was added to enhance the light emission, which is normally too faint for unaided photography.

cavities on the order of 5000 K. However, when Hiller et al. [4] and Atchley and co-workers [5] studied SBSL emissions, they discovered a smooth spectrum, devoid of any distinct bands. This suggests the presence of much higher temperatures, perhaps orders of magnitude greater than those encountered in MBSL systems.

To date, only one viable explanation has been offered for the short pulse duration of the SBSL flash and for the seemingly extreme temperatures involved: a

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spherically converging shock wave generated within the collapsing bubble. Wu and Roberts (7) as well as Greenspan and Nadim (8) have demonstrated numerically that such an imploding shock should exist in the SBSL bubble and that extremely short pulse durations (0.1 ps) and high temperatures (1000 eV; 1 eV = 11,600 K) should occur. Using a more accurate equation of state, Moss et al. (9) have confirmed predictions of extreme temperatures and pressures, obtaining values more in line with the (crude, at this time) experimental measurements, namely, pulse durations on the order of 10 ps and peak temperatures on the order of 10 to 100 eV. Furthermore, their computations suggest that at various locations within the imploded core at the center of the bubble, pressures can be as high as 200 Mbar (1 Mbar = 10^{11} Pa), and densities as high as 13.4 g/cm³ (at these levels, it is possible that the compressed air near the center of the bubble will have properties similar to that of a metal). Note that all the calculated results cited above are based on one-dimensional calculations assuming a perfectly symmetrical bubble collapse and are mitigated by the effects of dissociation and ionization [which are accounted for in the Moss et al. (9) computations] and by various radiation and mass transport mechanisms (which are not accounted for by Moss et al.).

As indicated in figure 2 of Hiller et al. (10), a small quantity of argon introduced into a pure nitrogen bubble increases the luminosity of SBSL by nearly two orders of magnitude. What effect does argon have on this system? Does it strongly influence the dissociation, ionization, and radiation transport within the core? Does it have a catalytic effect on electronic transitions within the plasma or material composing the core? Does it readily conduct heat from the hot interior of the core to the outer layers and thus increase the radiated energy or the total volume of high-temperature gas? These questions are difficult to answer with the existing data and clearly require additional measurements and computations.

Figure 3 of Hiller et al. (10) demonstrates that if the bubble contains certain gas species, the spectra show broad peaks near 300 nm, whereas for other species, no peaks exist and the spectrum monotonically increases down to the water cutoff (the transmissivity of the ultraviolet through water is greatly reduced below 200 nm). Why is it that a maximum exists at all? If the gas core is heated and compressed to the degree predicted by recent theories, then only the outer shell should radiate (like the sun). If there is a broad maxima for xenon, then shouldn't there also be one for helium? These again are anomalous results and perhaps have something

to do with the heat transport through the compressed gas.

Finally, the data displayed in figure 5 either have a trivial explanation (for example, a periodic detuning of the cell) or they are truly remarkable. These data suggest that some mechanism, possibly gas diffusion across the gas-liquid interface, is causing the luminosity and equilibrium bubble radius to cycle with a period on the order of seconds. It seems remarkable to us that such long-term memory (on the order of 100,000 acoustic cycles) could exist in a mechanical system.

As we currently understand it, single-bubble sonoluminescence may result in temperatures in excess of 10^5 K, pressures in excess of 10^7 bar, light emissions lasting less than 50 ps, and mechanical energy concentrations of up to 12 orders of magnitude; all this from a simple acoustical system costing a few hundred dollars to construct. It is a remarkable laboratory for physics and chemistry.

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SINGLE BUBBLE SONOLUMINESCENCE

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ABSTRACT If acoustic cavitation is produced in a liquid, the implosion of the cavities can heat the internal contents of the bubble to incandescent temperatures. The electromagnetic emissions associated with this energy concentration can often be seen with the naked eye. This phenomenon, in which light is generated by sound is called sonoluminescence. There are two kinds of sonoluminescence: one type is associated with the production of many cavitation bubbles by a sound field--this form is called multiple-bubble sonoluminescence; a second type is associated with the production of light from a single, stable, violently oscillating gas bubble--this form is called single bubble sonoluminescence. This latter form is much easier to study because the fundamental bubble dynamics that leads to bubble collapse and the associated electromagnetic emissions can be ascertained. Also, in single bubble sonoluminescence, it is likely that the bubble collapse is spherically symmetric, resulting in an amplification of this already violent phenomenon. This article presents a brief survey of single bubble sonoluminescence and describes some of more remarkable aspects of its behavior.

INTRODUCTION

When an acoustic wave propagates through a liquid, certain conditions can be attained in which the mechanical energy associated with the acoustic field is converted into electromagnetic energy. This process is called *sonoluminescence*, and is the principal focus of this article.

Sonoluminescence is the indirect consequence of a process called acoustic cavitation, in which the acoustic stress applied to the liquid causes the liquid to fail during the negative half cycle, producing vapor- and gas-filled voids within the liquid. The subsequent collapse of these voids during the positive half cycle can be sufficiently violent to produce sonoluminescence. When cavitation is generated in the bulk of a liquid, multiple cavitation "sites" usually appear with the result that the process is not localized at a particular point but spatially and temporally distributed over a relatively large parameter space. This cavitation takes on various forms, but at the moderate amplitudes of interest (0.05 - 0.50 MPa), one can observe many small bubbles; on an instantaneous basis, one sees random flashes of light from the SL zone that gradually build into a geometrical configuration representative of the acoustic field produced by the transducer and the constraining volume [Crum, et al., 1986; 1987].

SL was discovered nearly 60 years [Marinesco and Trillat, 1933; Frenzel and Schultes, 1935], and since then there have been a variety of explanations given for the origin of the electromagnetic emissions. Electrical discharge theories of various types were at first quite popular. As early as 1940, Frenkel [1940] suggested that electrical charges known to exist on the surfaces of bubbles (see for example, [Watmough, et al., 1992]) were somehow made to discharge. This model, though seriously challenged by the experiments of Suslick [Suslick, 1989;1990], even has it modern advocates [Margulis, 1992].

However, most modern researchers support the hot-spot model of Noltingk and Neppiras [1950] which posits SL to be the result of incandescence of the bubble's contents. Nonetheless, there are still many unanswered questions concerning the origin of this phenomenon.

One reason SL has intrigued investigators is its enormous capability of energy amplification. For example, an acoustic pressure amplitude of 0.1 MPa (1 bar) can generate sonoluminescence in water. This pressure corresponds to an acoustic energy density of about 2.2 j/cm^3 or, in a rather unconventional unit, to an energy density of about 4×10^{-10} ev/molecule. In contrast, there is recent evidence that the photons associated with SL can have energies in excess of 6 ev; thus, the generation of SL from an acoustic wave results in an energy amplification of approximately 1.5×10^{10}! To see how this compares with other phenomena, consider a thermal neutron that is absorbed by the fissionable isotope of Uranium. The neutron has about 0.025 ev of energy while the resulting fission releases about 200 Mev--an energy amplification of *only* 0.8×10^{10}.

It has been difficult to determine the basic physical processes that give rise to SL, partly because it is practically impossible to spatially and temporally control the production of cavitation, the origin of SL [Crum and Reynolds, 1985]. It occurs randomly and over a relatively large spatial area. However, the fortuitous discovery of SL from a single stable cavitation bubble by Gaitan, [1990] has now made it possible to study the phenomenon in much more detail than was previously possible. With this system the dynamics of a single cavitation bubble can be studied simultaneously with the physical processes that lead to SL, thus isolating the critical temporal and spatial parameters that give rise to SL [Gaitan and Crum, 1990; Gaitan, et al., 1992]. Furthermore, some recent discoveries associated with Single Bubble Sonoluminescence (SBSL) have been quite dramatic and totally unexpected; according, research into this phenomenon has potential for interesting new physics as well as important technology applications.


RESULTS

Single Bubble Sonoluminescence. In order to understand this phenomenon, it is first necessary to explain how one can generate the conditions under which it can be expressed.

If a gas bubble is positioned within an acoustic stationary wave, and driven at a frequency below it natural resonance frequency, it will experience radiation pressure forces, called Bjerknes forces [Crum, 1975], which will tend to force the bubble toward an acoustic antinode. Simultaneously, the bubble will also experience the buoyancy forces of gravitation which will normally be directed vertically upwards. Thus, under conditions that are not too difficult to obtain, it is possible to "acoustically levitate" a single bubble in the bulk of a liquid [Crum,1980; 1983]. Under conditions that ARE reasonably difficult to attain, it is possible to see SL from this single bubble. Shown in Fig. 1 is a diagram of an experimental arrangement that permits SBSL to be observed.

It is a rather dramatic sight to see a very small bubble that is a constant source of light emissions. When seen with the naked eye in a darkened background, it appears as a bright star, glowing brightly. When background lights are illuminated in the room, it is still possible to see the light emissions from the bubble. Even more remarkably, the bubble tends to remain firmly fixed in space, without any perceivable movement within the liquid. In our initial studies of this phenomenon, we wished to determine if the bubble remained a single entity during its entire oscillation cycle and thus conceived a light scattering technique for visualizing the bubble.

Fig. 1. A schematic diagram of the experimental apparatus used to acoustically levitate a gas bubble and to generate single bubble sonoluminescence. This figure also shows the apparatus used to record the electromagnetic emissions.
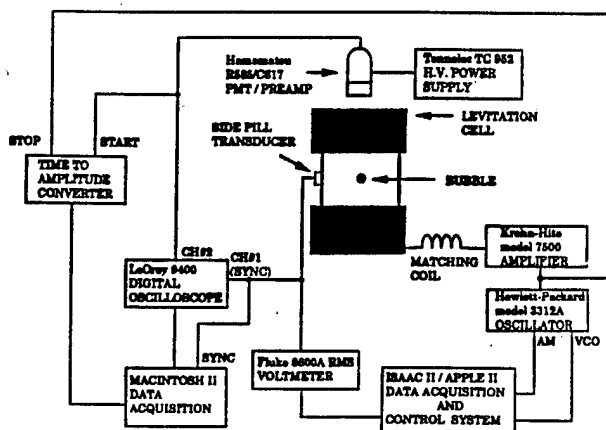
Shown in Fig. 2 is a diagram of the experimental system used to determine the radius-time curve of the single bubble. By using the apparatus shown in Fig. 2 and the techniques developed by Holt and Crum [1992], the data shown in Fig. 3. were obtained.

Fig. 2. A schematic diagram of the experimental apparatus used to scatter laser light from the sonoluminescing bubble and to obtain the radius-time curve.
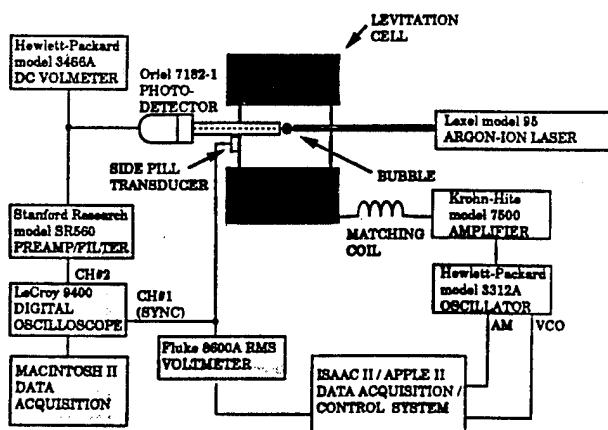
In Fig. 3 the acoustic field is shown in the top trace, the experimentally-determined radius-time curve in the middle trace, and the SL emissions in the bottom trace. Note that the emissions are synchronous with the collapse of the bubble, and that they occur each and every acoustic cycle.

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Fig. 3. Simultaneous plots of the sound field (top), the measured bubble radius (middle) and the sonoluminescence emissions (bottom). For this case the acoustic pressure amplitude was about 0.12 MPa, the driving frequency was 22.3 kHz, and the host liquid was a glycerin/water mixture.
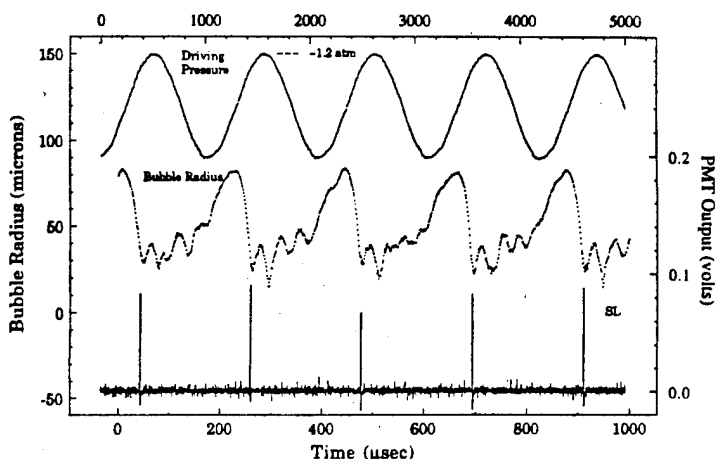
Although only a few acoustic cycles are shown in this trace, we have observed the behavior shown here to be repeated for hours.

Origins of Single Bubble Sonoluminescence. The fact that this system is very "robust" and the luminescing bubble tends to remain in a stable configuration was initially very difficult to understand. A gas bubble is a very nonlinear mechanical oscillator, and one would not expect it to behave in such a stable pattern. For example, consider Fig. 4, which shows the calculated response curves for the bubble as a function of its size and its driving amplitude. Note that for the bottom trace, even for a driving acoustic pressure amplitude of 0.06 MPa (0.6 bar), there is a very nonlinear response. Since the threshold for SBSL is approximately 0.1 MPa, and extends to abut 0.15 MPa, the two top curves on this figure illustrate the expected bubble response. Obviously, the bubble must behave in a very nonlinear fashion.

Fig. 4. Bubble response curves for various acoustic pressure amplitudes using the Keller-Prosperetti formulation of bubble dynamics [Prosperetti, et al., 1988]. For these curves, the liquid is assumed to be water, saturated with gas, and driven at a frequency of 21 kHz. R_o refers to the equilibrium radius; R_{max} to the maximum radius; R_{res} to the linear resonance radius of the bubble.


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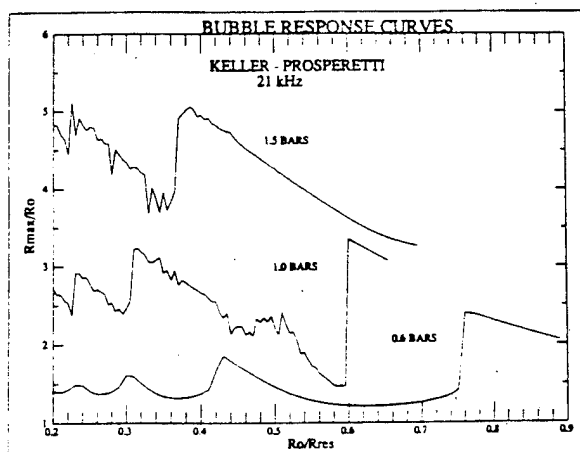
Another phenomenon associated with an oscillating bubble within a liquid that should affect the stability of this system is "rectified diffusion" [Hsieh and Plesset, 1961; Strasberg, 1961; Crum, 1980]. This effect also results from the nonlinear behavior of the bubble. Specifically, when the bubble is large, gas diffuses into the bubble; when it is small, gas diffuses out. Because the diffusion is proportional to the area, over a complete cycle, more gas diffuses in than out; thus, there is a "rectification" of mass into the bubble. The "area effect" is enhanced by the fact that a small shell of liquid surrounding the bubble is compressed during expansion, thus concentrating the dissolved gas near the bubble wall and enhancing the diffusion rate; just the opposite happens during compression. The combination of the "area effect" and the "shell effect" is to pump significant amounts of gas into the bubble each acoustic cycle.

Fig. 5. Shown here are experimental measurements that demonstrate the phenomenon of rectified diffusion. One sees that for the range of conditions observed in this experiment, it is possible to use an analytical theory to accurately predict the threshold and the magnitude of the bubble growth rate.
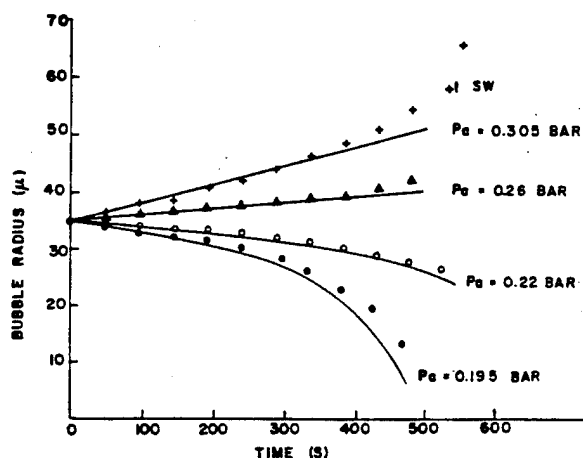
When one combines the effect of the nonlinear oscillations of a bubble and the concept of rectified diffusion, one can gain some insight into the probable origins of SBSL. Using the nonlinear rectified diffusion code developed by Church, [1988], we have investigated this phenomenon for bubbles under the set of parameters similar to those experiencing sonoluminescence. Consider Fig. 6, which shows the threshold for rectified diffusion under the conditions similar to those that would give rise to SL.

Fig. 6. Calculations of the threshold for rectified diffusion of gas bubbles in water for a driving frequency of 20.0 kHz and dissolved gas concentrations of 5% (solid line) and 100% (dashed line). Note that for this case, the threshold is so large that nonlinear behavior is observed.
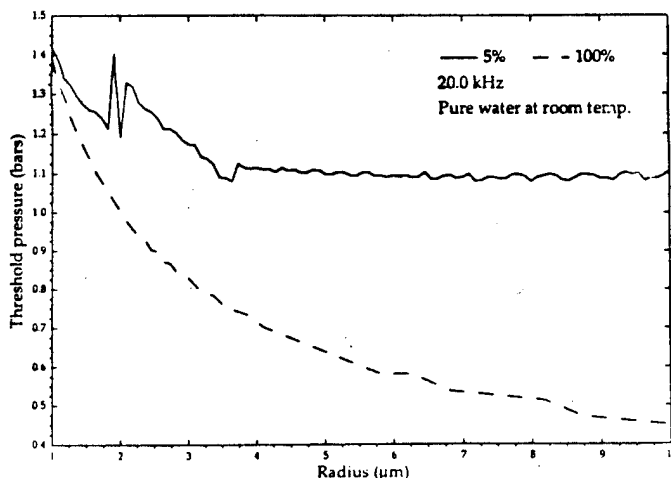
Note that when one reduces the dissolved gas concentration to the level desirable for SBSL, a couple of "notches" appear in the threshold curve that could be very meaningful (these notches or depressions or valleys are due to the nonlinear response of the bubble and represent harmonic resonances). Consider the notch near 3.5 μm; this value of the radius is near that of the value measured by Barber and Putterman [1993] in their light scattering experiments. Suppose that a bubble were "positioned" within this notch (above the threshold) by selecting a bubble of about 3.5 μm in radius and driving it at a pressure amplitude of 0.115 MPa (1.15 bars) and at a frequency of 20 kHz. This particular bubble would then grow until it engages the threshold curve at about 3.7 μm. At this point, if it grew further, it would pass into a region for which the threshold is higher than 0.115 MPa, and it would start to dissolve. As it got smaller, it would cross the threshold line once again, and get larger, etc. Thus, a positive slope on the rectified diffusion threshold curve is a point of stable equilibrium for a bubble driven at a fixed acoustic pressure amplitude.

For this bubble to produce SL flashes each cycle, it would seem necessary that shape oscillations not occur, because that should lead to asymmetrical bubble collapse, which would in turn, tend to prevent SL. It is difficult to make measurements in this region, of course, but the extrapolations of our earlier measurements and calculations [Horsburg, et al., 1989] suggest that the threshold for shape oscillations is larger than 0.115 MPa in this radius range (2-5 μm). Thus, it is plausible that this general region of parameter space is the location for single-bubble sonoluminescence.

Unique Aspects of SBSL. Putterman and his colleagues [Barber and Putterman, 1991; Barber, et al., 1992; 1994; Barber and Putterman, 1992; Hiller, et al., 1992] have examined various aspects of SBSL and determined that the phenomenon itself has some amazing and unique features. For example, the lifetime of the flash appears to be no longer than 50 ps. Since one would expect that this lifetime would be associated with the time for which the gas in the interior was heated to incandescent temperatures, it would seem possible to calculate the emission time. Although we have not performed these calculations specifically for the case of SBSL, we can learn from the computations of Kamath and Prosperetti [Kamath, et al., 1993] that elevated temperatures are expected to occur for times on the order of nanoseconds. The only explanation (at this time) for the short lifetime of SBSL is that an imploding shock wave is launched within the gas during the final stages of bubble collapse and this shock wave gives rise to these emissions [Barber, et al., 1994].

A second phenomenon discovered initially by Gaitan [Gaitan, et al., 1988] but refined in considered detail by Barber and Putterman [1991] is the remarkable stability of the luminescing bubble. If one measures the jitter in the SL emissions from cycle to cycle, under normal conditions, this jitter is itself on the order of 50 ps. This level of stability is much in excess of the electrical apparatus that drives the system. There is no current explanation for this behavior.

Finally, since the optical emissions from SBSL are sufficiently intense so that one can obtain a spectrum, it is of great interest to use this spectrum to obtain a measure of the effective temperature of the gas within the collapsed (imploded) bubble.

Shown in Fig. 7 is a spectrum obtained by Carlson, et al., [1993]. Because the spectrum, as shown in this figure, seems to be best-fit with a black body curve, one could estimate the effective temperature of the SL emissions by the best-fit-black-body tempera-

ture. As shown on this figure, this value can be as high as 16,000K--a rather remarkable value, considering the surface of the sun is only about 7,000K!

Fig. 7. Spectrum of light emitted by single bubble sonoluminescence. The heavy line is the measured spectrum; the light line is the best fit to the spectrum using a black body distribution function. [After Carlson, et al., 1993].
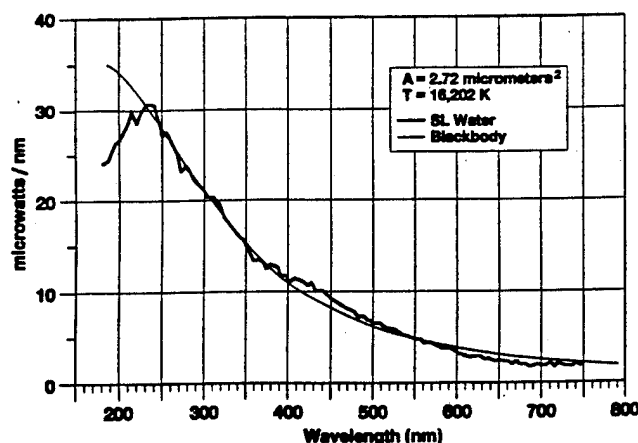
SUMMARY

Single bubble sonoluminescence is a remarkable phenomenon that is largely not understood. The bubble demonstrates a stability that is totally unexpected; the duration of the sonoluminescence emissions are so short as to be unmeasurable with currently available apparatus, and the emission spectrum shows indications of extraordinarily high temperatures. This phenomenon bears further study, both from an experimental and theoretical aspect.

ACKNOWLEDGMENT

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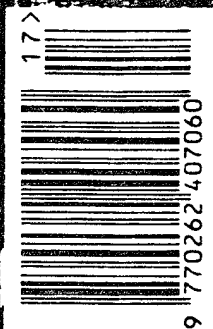Suslick, K. S. "Sonochemistry", Science **247**, 325 (1990).

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Molecular movies

When planes fall
out of the sky

Bubbles hotter than the Sun

Bubbles hotter than the Sun

Hit water with a blast of sound and tiny bubbles start to glow. This astonishing phenomenon has enormous potential, says *Lawrence A. Crum*

TAKE a jar of water, pass sound waves through it and, hey presto, it gives off light. How can this be? For one thing, visible light has so much more energy than sound waves that to turn sound into light you would have to boost the sound's energy a trillionfold, roughly equivalent to focusing all the sunlight striking the Earth onto about 100 square metres.

It turns out that when sound waves are passed through water, they generate tiny bubbles that are expert at focusing energy. And in the process, these bubbles can reach temperatures that are hotter than the surface of the Sun and pressures tens of thousands of times that of the Earth's atmosphere, opening the way to exotic chemical reactions using astonishingly simple equipment (see Box "Sounding out chemistry"). And researchers now suspect that they may get hotter still—perhaps even hot enough to achieve the elusive nuclear fusion.

Sonoluminescence, the process of turning sound into light, was discovered over 60 years ago, but it was not until 1959 that Erwin Meyer and Heinrich Kuttruff from the University of Göttingen in Germany, discovered that the light came from the collapse of tiny bubbles produced by the sound field, a process called acoustic cavitation.

Concentrated energy

Bubbles can unleash extraordinary amounts of energy when they collapse; for example, if water passes over an obstruction such as a ship's propeller or a turbine blade, bubbles can be generated which, when they collapse, can punch a hole in solid brass or steel. But the concentration of energy needed to turn sound into light is even higher than this.

Sound waves are simply pressure waves alternately compressing and expanding the medium through which they move. Imagine what happens if they pass through liquid. When the pressure drops the liquid effectively boils, forming a bubble that begins to expand, and when the pressure rises again the bubble is forced to collapse. At this stage, the gas inside it is greatly compressed and heated to a very high temperature, and light is emitted.

In 1986, Ken Suslick at the University of Illinois used chemical rate equations to infer that collapsing bubbles in a sound field could reach temperatures of around 5000 K. In 1993, using sophisticated computer models of bubble collapse, Andrea Prosperetti of Johns Hopkins University in Baltimore calculated even higher temperatures of around 7000 K, approximately the temperature of the surface of the Sun, and higher than the temperature of an acetylene torch used to cut hardened steel. Chemists were thrilled at the prospect of such high temperatures from such simple equipment—a jar of liquid and a sound field. Even though the overall temperature of the liquid stays about the same, there are many thousands of tiny gas bubbles that reach temperatures of thousands of degrees, which makes it possible to break apart molecules and produce chemical reactions that would otherwise be very hard in an ordinary laboratory.

Meanwhile, physicists have been trying to understand exactly how sonoluminescence works. One clue comes from the way the light emissions are distributed, sometimes evenly throughout the water, and sometimes concentrated as intense bands of light at certain points. It turns out that these intense bands coincide with the regions where sound is most intense, in the acoustic "standing waves". These are combinations of forward and reverse waves that look like a single stationary wave, and that occur when a wave moving in one direction is reflected back from a boundary.

But whether it is concentrated in the bands or not, the light comes from so many different parts of the liquid that it must involve the collapse of many different bubbles. And any attempt to understand what is really going on in more detail runs up against the problem that this multiple bubble sonoluminescence is just too messy—imagine trying to understand what is happening in a thousand different bubbles, emitting light at different places.

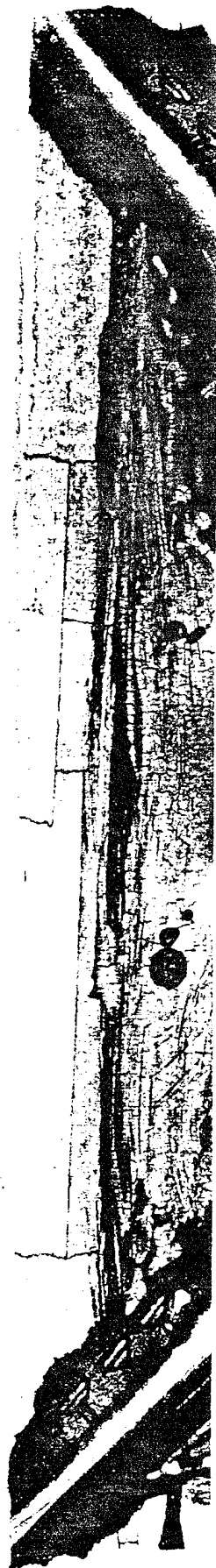Fortunately, in 1990 Felipe Gaitan, a graduate student at the University of Mississippi

SONO

HOT

LUMINUS

As a bubble in a liquid is forced to collapse by a passing sound wave, a shock wave is launched which heats the molecules at the centre of the bubble to enormous temperatures and causes them to give off light

managed to come up with a way out of the messiness when he devised a simple system containing a single "levitated" sonoluminescing bubble. If there is an acoustic standing wave in the middle of the liquid, the forces associated with this standing wave try to move the bubble towards the strongest part of the sound field—that is, towards the middle of the container.

But the bubble is also trying to rise to the surface of the liquid because of its inherent buoyancy. Gaitan tweaked the sound field until the two forces exactly balanced, and levitated the bubble at a fixed position in the liquid. By reducing the amount of gas that was dissolved in the liquid, he could force a single bubble to grow and collapses reaching a bigger size during each successive cycle. Eventually, he found just the right conditions and the bubble glowed like a tiny star.

'The temperatures in the imploded shock wave could still reach 2 million degrees, roughly half of what is needed for fusion'

The discovery of single bubble sonoluminescence (SBSL) made it possible to study sonoluminescence in much more detail than before. By scattering light from a laser beam off the bubble, we watched the violent oscillations, and discovered that, true to our expectations, the light flash was emitted when the bubble imploded. More surprisingly, though, the bubble didn't destroy itself when it collapsed, but reappeared out of the ashes of the implosion.

There were other surprises in store. According to Prosperetti's calculations, the light flash should last about 20 billionths of a second. But in 1991, Seth Putterman and his colleagues at the University of California, Los Angeles, had shown that Pros-

peretti's predictions were out by a factor of a thousand. They discovered that the light flash lasted for less than 50 trillionths of a second, and the spectrum of the emitted light seemed to show that the temperature inside the bubble was not thousands of degrees, as suggested by Prosperetti, but tens of thousands.

In his calculations, Prosperetti had assumed that when the bubbles collapse, the gas inside is compressed by thousands of times its normal pressure, heating it dramatically. This, he believed, would cause the gas to give off light to shed its newly acquired energy. His calculations and our light-scattering experiments showed that the bubble takes about 20 billionths of a second to collapse, so he assumed that the gas would be heated for the same length of time. But if the hot gas is responsible for the light flash, why should the flash be so much shorter than the time the gas is heated? And why should the temperature be so much hotter than predicted?

One possible explanation is that the inside of the bubble is not heated all at once. Back in 1960, Peter Jarman, an Australian physicist, suggested that a shock wave developed inside the sonoluminescing bubble and that this was responsible for heating the gas. At the time there was no evidence to support this, and Jarman's views were largely ignored. But in the light of Putterman's 1991 experiments and some more recent research by Mike Moran and Willie Moss of the Lawrence Livermore Laboratory in California many physicists began to wonder whether Jarman was right after all.

Two years ago, Cheng Chin Wu and Paul Roberts of UCLA tried to work out what would happen to the gas if a shock wave were created. They assumed that things behave more or less according to Prosperetti's theory until the final stage of collapse. By then, the outside of the bubble could be moving towards the centre faster than the speed of sound, which would launch a shock wave into the centre of the bubble, in much

Sounding out chemistry

NEARLY seventy years ago, Princeton scientist Alfred Loomis first noticed the chemical effects of ultrasound—sound waves whose frequency is too high to be audible to humans. But the field of sonochemistry lay fallow until the 1980s when inexpensive and reliable laboratory generators of high-intensity ultrasound became available.

Sonochemistry occurs because of acoustic cavitation—the formation, growth, and implosive collapse of bubbles in a liquid irradiated with high-intensity sound or ultrasound. The collapse generates intense local heating and extreme pressures, but for very short timespans, typically less than a millionth of a second.

Because the bubbles are tiny, the hot regions that they generate then cool very rapidly, at rates of more than 10^{10} degrees per second—a million times faster than cooling a red-hot metal poker by plunging it into ice water. The immense local temperatures and pressures and the extraordinary heating and cooling rates generated by the collapsing bubble mean that ultrasound is an extremely unusual and potentially very useful method of generating high-energy chemistry.
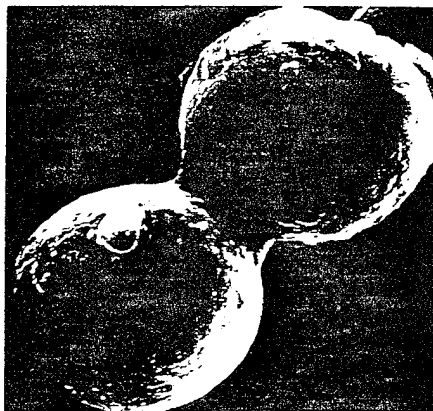
One of many exciting applications of sonochemistry lies with amorphous metals. If a molten metal alloy can be cooled quickly enough, it can freeze into a solid before it has a chance to crystallise properly. Unlike normal metals or alloys, the resulting amorphous alloys have no crystalline structure on a scale of more than a few hundred atoms. They thus can have unique

Collapsing bubbles cause tiny particles of metal powder to crash together and fuse

electronic and magnetic properties, and can also resist corrosion, but are hard to make because the cooling has to be very rapid.
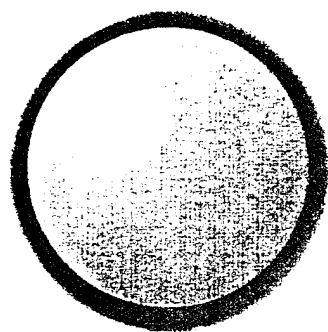
In 1992, three researchers in my group at the University of Illinois managed to capitalise on the rapid cooling rates that sonochemistry offers. Seok-Burm Choe, Andrzej Cichowlas and Mark Grinstaff used ultrasound to decompose solutions of organometallic compounds and create hot clusters of metal atoms, which amalgamated and cooled very rapidly to form amorphous metal powders made up of nanometre-sized metal clusters.

This means that it may be possible to make unusual materials at low overall temperatures. For example, we used iron pentacarbonyl to produce amorphous iron, which has a very high surface area and is an active catalyst for several important reactions, for example converting carbon monoxide from coal into liquid fuel. And magnetic measurements reveal that the amorphous iron is a very soft ferromagnet—in other words, it quickly forgets its original magnetisation and adopts a new one when a magnetic field is applied. Such materials are excellent for electrical trans-
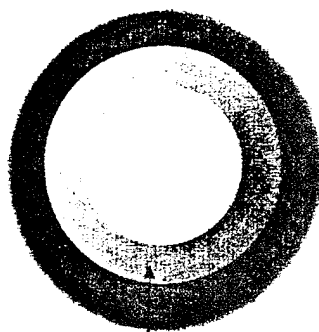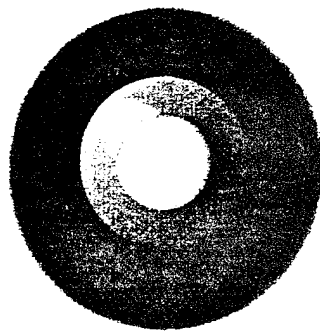
Collapsing air bubble | Imploding shock wave | High temperature | Light emission

the same way that Concorde's supersonic speeds generate sonic booms. As the molecules in the shock wave all try to arrive at the centre of the bubble at once, they bounce against one another causing the shock wave to rebound. During the implosion, the gas at the centre is heated, but when the shock wave rebounds it allows the gas to expand and cool very rapidly.

Wu and Roberts decided that the gas would therefore be heated for only a very short time, in line with the experimental measurements of the flash duration. They also realised that the energy generated when the bubble collapsed would be distributed over a much smaller volume than had been assumed previously—only the molecules in the very centre would be affected. This would give a higher concentration of energy, and therefore higher temperatures. Wu and Roberts decided that shock waves were the answer, explaining both the rapid flash and the high temperatures seen in experiments.

Noble mystery

Investigations of SBSL have also raised plenty of new questions. For example, in October last year Robert Hiller, from Putterman's group at UCLA, reported in Science that the presence of noble gases such as argon, helium or xenon seemed to be crucial for the sonoluminescence. They discovered this almost by accident. When they filled their luminescing bubble with air

they saw plenty of light, but when they filled it with nitrogen or oxygen—the two main constituents of air—there was hardly any light. They realised that air contains a small but significant impurity of argon and so they tried adding a small amount of argon to the nitrogen. To their surprise, they discovered that a mixture containing just 0·1 per cent argon boosted the luminosity by a factor of nearly 30. Helium or xenon worked just as well. For now, no one knows why a small amount of a noble gas should produce such a dramatic change.

Meanwhile, the extreme conditions created during sonoluminescence have raised the exciting, albeit highly controversial idea that SBSL could be used to create nuclear fusion. Nuclear fusion is the energy source that drives the Sun and other stars. Deep inside the Sun, where the gravitational force is enormous, the nuclei of deuterium, a heavy isotope of hydrogen, are forced to fuse to form helium nuclei, releasing tremendous amounts of energy in the process. For many years, physicists have been trying to produce controlled fusion on Earth, because hydrogen is so plentiful here that this could provide a virtually unlimited energy source. But although billions of dollars have been spent on fusion research, we are still at least twenty or thirty years from a commercial process.

The main problem is that before fusion can take place the temperatures and pressures must be extremely high, conditions

former cores or magnetic recording heads.

At the other end of the scale, sonochemistry's extreme temperatures could also benefit industries or governments struggling to clean up water sources contaminated by small amounts of halocarbons, pesticides, or other toxic or carcinogenic compounds. Everyone knew that applying ultrasound to aqueous solutions yielded hydrogen and hydrogen peroxide, but Peter Riesz at the US National Institutes of Health recently proved that aqueous sonochemistry also yields the hydroxyl radical, which is an extremely potent oxidising agent normally formed in flames. In other words, the high temperatures of cavitation create flame-like conditions inside the liquid water, breaking the water's hydrogen-oxygen bond and forming the hydroxyl—normally a very difficult feat.

Other researchers have also been hard at work in similar areas. Over at the Hahn-Meitner Institute in Berlin, Arnim Henglein's team has turned up many other similarities between sonochemistry and combustion chemistry, and Michael Hoffmann at the California Institute of Technology is exploring applications for these ex-

tremely high-energy chemical reactions for cleaning up contaminated water supplies.

High-intensity ultrasound can be used to increase the speed of reactions at metal surfaces substantially, and this has become an important synthetic technique for many chemical reactions, especially those involving reactive metals such as magnesium, lithium or zinc, which are particularly important for synthesising pharmaceuticals and rare chemicals. This approach was first advocated by Pierre Renaud in France in the 1950s, and has been developed more recently by Jean-Louis Luche at the University of Toulouse.

Chemists are also excited by the shock waves generated when the bubbles collapse. These are like tiny depth charges in the liquid. If they occur in the presence of metal powder, they can smash nearby powder particles together at such high speeds that the particles actually melt at the points where they collide. This was discovered in 1990 by Stephen J. Doktycz and Dominick Casadonte in my group at the University of Illinois. Such collisions can produce striking changes in surface texture, composition, and reactivity of the powders.

Recently, Gareth Price at the University of Bath has been studying how to use sonochemistry to break up polymers dissolved in organic solvents. The polymer chains are split mechanically by shock waves when the solvent is irradiated with ultrasound. Price has used this to synthesise block copolymers, long-chain polymers with two or more different, but linked, parts—like a train made up of passenger cars in front and freight cars at the back. The idea is that block copolymers can combine the useful properties of their constituent parts.

Ultrasound is also useful for synthesising biomaterials, particularly micrometre-sized spheres with shells made from protein molecules that are bonded together sonochemically. Such microspheres are smaller than red blood cells and can be used to carry drugs and medical imaging agents through the bloodstream. One recent example is the use of high-intensity ultrasound by Mike Wong, a student at Illinois, to make long-lived haemoglobin microspheres suspended in water, which could act as a blood substitute to carry oxygen from the lungs to the rest of the body (Technology, 17 December 1994). **Kenneth S. Suslick**

that are very difficult to reach and control. Could they be reached in sonoluminescence? Using the shock-wave model, Wu and Roberts calculated that temperatures in SBSL could be as high as 100 million degrees. But this was for a highly idealised situation and not expected to be borne out in the laboratory, since Wu and Roberts had to make assumptions about the way gases behave at high temperatures and pressures.

But last November, at a meeting of the Acoustical Society of America in Houston, Moss reported more realistic calculations. He used sophisticated computer codes that use equations to represent the behaviour of gases under extreme conditions. To everyone's surprise, he reported that the temperatures in the imploded shock wave could still reach 2 million degrees—roughly half of what would be needed for fusion. What was more, the pressures would be so enormous—probably millions of atmospheres—that the density of the gas could reach that typical of metals.

Moss pointed out that while these astonishing temperatures and pressures are not high enough for nuclear fusion, it might be possible to increase the temperatures and pressures further. One way would be to apply an impulsive force or boost to the bubble just before the shock wave is launched into the gas, and thereby obtain much greater compression.

Achieving fusion from sonoluminescence seems rather remote, but there are various other approaches that might just work. For example, the system that is currently used to produce SBSL runs at a frequency of tens of thousands of cycles per second, so the bubble giving out the light has very little time to grow before it is forced to collapse. A lower frequency should create bigger bubbles and perhaps more compression.

Large bubbles may be too distorted by gravity to collapse in a spherically symmetrical way, and because this means the energy of the collapse will not all be focused in the centre, it would limit the ultimate temperature reached. But if an SBSL system were to be built in a gravity-free environment, such as a space station, it might be possible to overcome some of the limitations imposed by gravity on Earth, and use space to help us achieve temperatures and pressures high enough for fusion.

Even if none of these possibilities finally comes off, it seems likely that the extraordinary conditions generated during sonoluminescence will open up many exciting new avenues in years to come. □

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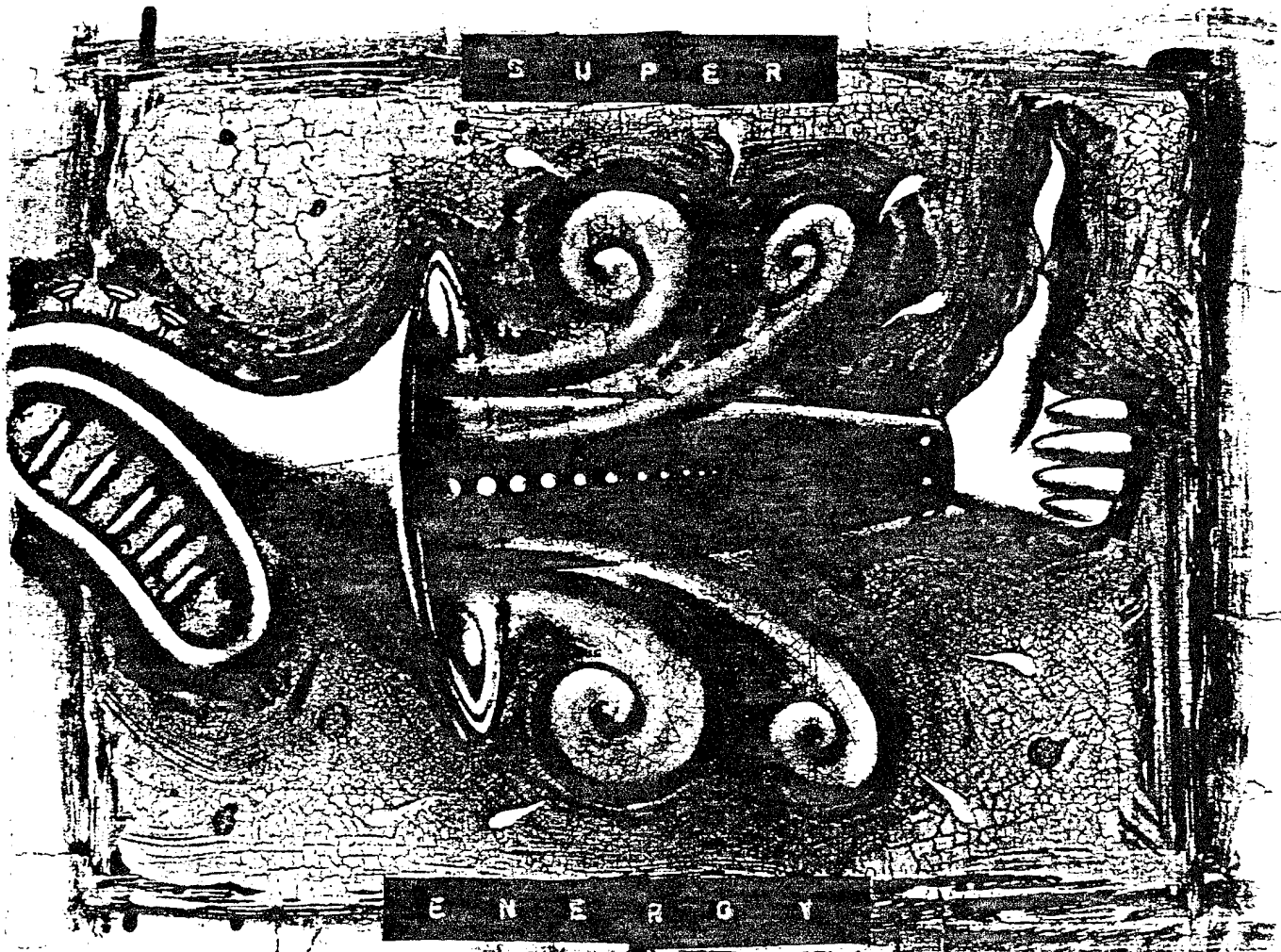
Comments on the evolving field of sonochemistry by a cavitation physicist

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Sonochemistry is an evolving field that has shown recent rapid growth and increasing interest. Although this field concentrates on chemistry and uses acoustics principally as a tool, the basic mechanism that gives rise to sonochemistry – acoustic cavitation – is often ignored or given little attention. This paper addresses some of the relevant aspects of cavitation and physical acoustics that apply to sonochemistry.

Keywords: sonochemistry; cavitation; bubble dynamics

The field of sonochemistry has existed for over 50 years and excellent work has been steadily produced by a variety of investigators. However, there has been a recent upsurge of interest in the topic, brought about particularly by some exciting scientific developments[1-4]. A prime example of the evolution of this field is the efforts toward the development of a scientific community, notably the European Society of Sonochemistry, which has now had four highly successful meetings. This particular paper reflects on the subjective views of one individual who attended the most recent meeting held in Blankenberg, Belgium, and presented a plenary paper at that meeting.

Acoustics

The developing field of sonochemistry has an interesting parallel with that involving the medical and biological effects of ultrasound. In early papers on this topic, it was not uncommon to see research articles that described a particular bioeffect in great detail but a limited and incomplete description given of the acoustic system that gave rise to that effect. Because it was generally difficult to duplicate such experiments in other laboratories, this inadequate description of the acoustic field soon resulted in the insistence by editors and reviewers that their deficiency be remedied. Currently, it is difficult to have a bioeffects paper accepted in a major journal without a full description being given of the characteristics of the acoustic field that gave rise to such an effect.

Currently, most sonochemistry reaction vessels are designed by chemists, with an emphasis on facilitating the chemistry rather than simplifying the acoustics. Consequently, these systems are mechanically complex and difficult to model from an acoustics perspective. Moreover, these systems are designed to produce a particular yield in a minimal time and thus tend to seek acoustic sources

that provide high acoustic power into small (and often geometrically complex) volumes. Further, a probe hydrophone that would be used to characterize acoustically such systems suffers the destructive effect of this mechanically and chemically active region. Efforts to develop instrumentation for the acoutic characterization of such systems have met with similar lack of success. Nonetheless, it is extremely important that the acoustic systems that give rise to sonochemistry be characterized in as much detail as possible.

Cavitation and bubble dynamics

It is generally assumed that sonochemistry cannot occur without cavitation. Although it is clear that acoustic cavitation plays a major role in most of the sonochemical reactions studied, it is also clear that there are cases in which the high intensity ultrasound acts principally to increase convection (an ultrasonic stirrer); accordingly, it is possible that cavitation, in such cases, is undesirable and actually reduces yields. Of course, Luche *et al.*[5] contend that this is not 'true sonochemistry'; nevertheless, it is often difficult to determine when cavitation is involved and when it is not. Further, it seems reasonable to assume that there will be many cases in which both the mechanical and the chemical effects of cavitation are important in reaction yields. In order that this field can advance, efforts to determine the existence and intensity of cavitation should be given high priority. We turn now to the important phenomenon of cavitation.

Hot spot or not!

The concept of a 'hot spot' as a necessary ingredient of sonochemistry was originally conceived by Noltingk and Neppiras[6] and has more recently been promoted by

Suslick et al.[7] Of course there have been a variety of alternative explanations, most notably those involving various electrical hypotheses, in particular those of Margulis[8] and LePoint and Mullie. and

It is important to recognize that the very nature of (violent) acoustic cavitation demands a hot spot. Whenever acoustic pressure amplitudes in excess of about 0.1 MPa exist in a liquid that is saturated with gas, there is a rapid growth of the equilibrium size of the bubble during the rarefaction phase of the sound field, to volumes at least one (and usually several) order(s) of magnitude larger. (By equilibrium size, it is meant the size in the absence of the bubble of a sound field). Thus, there is considerable potential energy supplied to the expanded bubble by the acoustic source. Again, by the very nature of acoustic cavitation, this the potential energy is converted to kinetic energy in a very short time period (i.e. short with respect to the period of the acoustic field, which is itself fairly short). Consequently, such a collapse cannot be isothermal, even for liquid metals with large thermal conductivities, but rather must be adiabatic. Finally, the relatively small volume of gas contained within the initial nucleation site, and the relatively long times required for gas diffusion from the liquid into the bubble, require that this fluid volume be relatively small (volumes of the order of microns cubed!). Consequently, acoustic cavitation results in an amazing degree of energy concentration, reported by some to be as high as eleven orders of magnitude[10]. Thus, even though there may be a variety of mechanisms for chemical kinetics, there must be a hot spot. It is simply reasonable to assume that this region of high temperature and pressures is the origin of chemical reactions.
there there

Homogeneous sonochemistry

In many sonochemical reactions, the majority of chemical activity occurs in the bulk of the homogeneous liquid. In this case, the cavitation field is likely to be composed of many active cavitation bubbles that grow from a variety of nucleation sites to sizes large with respect to these sites, a pictorial representation of this form of cavitation is shown in Figure 1(top).

Since an air–liquid interface is unstable under compression (this effect is generally described as a Rayleigh–Taylor intability and explains why the surface of ocean has waves when the wind blows), a bubble that collapses from an initially spherical configuration must eventually become unstable to surface instabilities sometime before it reaches minimum size. [Of course, there appears to be a rare and intriguing exception to this rule, evidenced by single-bubble sonoluminescence (SBSL), which will be discussed below.] These asymmetries are likely to be enhanced by neighbouring bubbles in a multi-bubble cavitation field, and evidenced by multiple bubble sonoluminescence (MBSL), but nonetheless will occur also in bubbles isolated from other bubbles or boundaries. Consequently, microscopic jets of liquid will be injected into the interior of the collapsed bubble. It is likely that these jets will often break up into microscopic droplets thaat have large surface/volume ratios. An example of such behaviour is shown in Figure 1a in a recent publication[11].

It is important to recognize that if a bubble did remain spherically symmetric throughout its collapse and rebound cycle, computations by Prosperetti and co-workers[12,13] indicate that sonochemitry would occur only within the vapour phase because (a) the liquid has a large heat capacity compared with the gas, (b) the thermal conductivity of liquids is also large, compared with that of most gases, (c) the total energy existing within a collapsed cavitation bubble is relatively high but absolutely low (measured in units of MeV, rather than joules or ergs)[14]. Accordingly, temperature rises only in the tens (or perhaps hundreds) of kelvins are to be expected. In contrast, for microscopic jets and droplets that are injected into the collapsed bubble interior, the temperature rise can be shown to be fairly large. A sample calculation illustrates this effect.

Suppose a collapsed cavitation bubble results in the generation of 300 MeV of total thermal energy created by a transient-cavitation collapse[14]. If 30 droplets of water of initial radius of 1.0 μm are contained within the collapsed bubble, and only 10% of this energy is used to raise the temperature of these droplets to superheated vapour, then a simple application of Joules' law results shows that in a temperature increase of 10 000 K, is expected for this vapor.

Heterogeneous sonochemistry

Whenever cavitation bubbles collapse in the vicinity of a surface, the asymmetry of the hydrodynamic flow field of high velocity results in a preferential geometry for jet development. For both hard and soft (pressure-release) boundaries, a liquid jet is generated that is directed toward the surface. This well known phenomenon[15] with visible liquid jets striking the boundary has demonstrated that enormous energy density is deposited at microscopic sites on the bubble surface; see Figure 1 (middle). However, not only mechanical dmage is produced by the impacting jet; for example, it has also been demonstrated that sonoluminescence (SL) is also produced from the vortex ring that results as a topological residue of the asymmetric collapse[16]. The eventual collapse of this ring can result in free radical production in the near vicinity of the solid surface, a rich region for sonochemical reactions.

A second aspect of cavitation bubble collapse near a boundary that is often neglected is the intense microstreaming that results from bubble pulsation. If liquid flow occurs near a plane boundary, a viscous boundary layer develops that is related to the liquid viscosity and the velocity of the flow. The thickness of this boundary layer is inversely proportional to the square root of the velocity[17]. For flow velocities typical of a mechanical stirrer, say $r = 1$ cm s^{-1}, this boundary layer can be of the order of hundreds of microns. For the surface to act as a catalyst for a particular chemical reaction, diffusion through this layer must occur. Since diffusion is an inherently slow process, this boundary layer probably presents an important limit to the rate of chemical reactions.

Suppose, however, that acoustic cavitation can be caused to occur near the surface of a catalyst or reacting surface. According to the observation of Elder[18], intense microstreaming can occur around bubbles located on the surface of the boundary. This microstreaming will dissipate the boundary layer in the vicinity of the bubble, and this chemical species can be rapidly convected to the thus surface of the catalyst. This microconvection should be very effective in increasing the reactivity of a catalyst. Of course, this effect, even though it involves c on, is not 'true sonochemistry' according to Lu [15], because it does not involve electron exchange s.
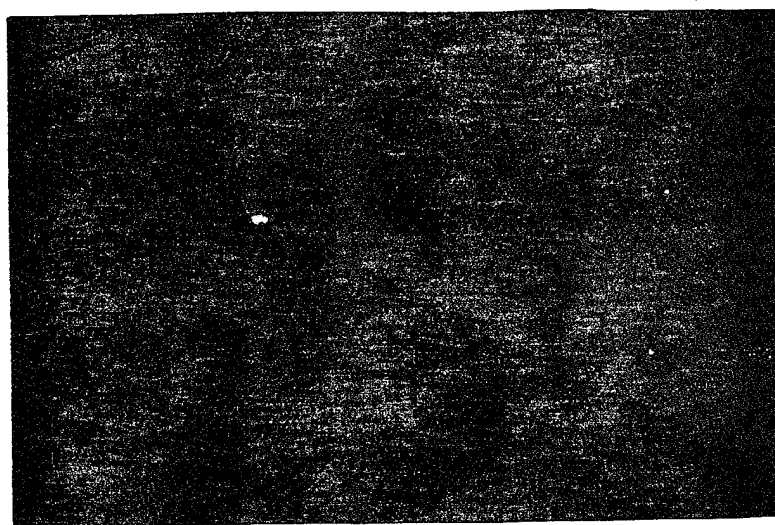
(a) **Homogeneous Sonochemistry**

(b) **Heterogeneous Sonochemistry**

(c) **Single Bubble Sonoluminescence**

Figure 1 (a) Homogeneous sonochemistry: because the liquid surrounding a cavitation bubble is a large heat sink, the temperature of the gas-liquid interface can be elevated only slightly[13]; however, if microdroplets or microjet filaments are inserted into the hot bubble interior, as shown, the liquid phase can be elevated to high temperatures. (b) Heterogeneous sonochemistry: when a cavitation bubble collapses near a boundary, (either soft or hard), liquid jets develop that impact the boundary (left) and cause damage to the surface[15] (right) These jet impacts can remove surface coatings, convect liquid readily to the surface and produce localized high temperatures and pressures. (c) Symmetric bubble collapse: in rare circumstances, cavitation bubbles can collapse symmetrically, generating high temperatures and pressures at the very centre of a cavity. This photograph shows a time exposure of single-bubble sonoluminescence[19], showing the maximum size of the bubble (approximately 100 μm in diameter) and light emissions from the geometric centre .

cavitation-induced microconvection may play an important role in influencing the yield in heterogeneous sonochemistry.

Symmetric bubble collapse

As indicated earlier, the compression of a liquid–gas interface is inherently unstable and any perturbation in the radial dimension can grow without bound. There appears to be a rare phenomenon that occurs within a relatively small parameter space in which this asymmetric collapse is somehow prevented; see *Figure 1* (bottom). In studies of SBSL[19,20], it appears as if an imploding shock wave develops within the gas contained within the collapsing bubble. It has been conjectured that this shock wave terminates further collapse of the liquid–gas interface and prevents asymmetric bubble collapse from destroying the bubble's geometric integrity. Although these speculations have yet to be firmly tested, they appear to be the only plausible explanations for the short SL pulse durations and high level of synchronicity observed in SBSL.

Although the phenomenon of SBSL is due to its many extraordinary features, suggests that its limited parameter space it probably plays a minor role in sonochemistry. However, the use of this well controlled phenomenon to study various aspects of the sonochemical reactions itself could be of some utility.

Other cavitation considerations

Frequency dependence. In theory a cavitation bubble grows during the negative portion of the acoustic cycle and is forced to collapse by the positive portion. Except for frequencies in excess of a few megahertz, such behaviour is approximately followed. For similar acoustic intensities and pressure amplitudes, this behaviour would suggest that cavitation bubbles at low frequencies (say, 20 kHz) would grow for about one half cycle or about 25 μs. Similarly, cavitation bubbles at high acoustic frequencies (say, 1 MHz) would have only 0.5 μs for growth. These significantly different times for growth result in small maximum sizes at high frequencies and thus less violent collapses. On the other hand, because there are more acoustic cycles at higher frequencies, there are more cavitation collapses and, thus, presumably more free radicals produced. This increased free-radical yield at higher frequencies is mitigated somewhat by the fact that the cavitation threshold increases with increase in frequency. It would seem reasonable to assume that cavitation collapses would be fewer but more violent at lower frequencies, and more frequent and less violent at higher frequencies. Thus, if a particular reaction is favoured by larger numbers of radicals, high frequencies should be desirable. Conversely, if the reaction is favoured by higher temperatures and pressures, then low frequencies are probably desirable. There are recent reports[21] of a nearly 30-fold increase in the oxidation rate of iodide when the frequency was increased from 20 to 900 kHz; is this evidence in support of arguments presented above? It would be useful for sonochemists to report reaction rates as a function of frequency, for equivalent acoustic intensities, to test this simple hypothesis.

Shock waves. It was shown by Vogel and Lauterborn[73] that shock wave amplitudes of the order of kilobars could be developed within the liquid by cavitation bubbles ●

induced. Further, since white noise is associated with impulsive sources (such as shock waves), the presence of extensive white noise at low frequencies (the audible 'frying' sound) indicates the likely presence of extensive shock waves. It is noted that cavitation at high frequencies has significantly less audible white noise, and thus probably less shock waves (both in number and in intensity). Since shock waves provide a potentially useful reaction-enhancement mechanism, it would be of interest to attempt experiments that would ascertain the role (if any) of shock waves in sonochemical yields.

Cavitation clouds. A cavitation area probably contains many individual cavitation bubbles. It is known from studies in ocean acoustics[23] that bubble clouds can act as discrete entities with a different sound speed velocities (in cases of large numbers of bubbles, this sound speed reduction can easily be an order of magnitude). Accordingly, clouds of bubbles can act as efficient scatterers of acoustic energy and can cause significant modification of the acoustic impedance provided to the acoustic source. In exceptional cases, it can even result in an effective decoupling of the source and the liquid medium.

Because bubble clouds are composed of individual pulsating bubbles, they can acoustically interact with each other. In studies of cavitation bubble dynamics, it is known that clouds of bubbles can collapse in such a cooperative manner that they develop cavitation jet velocities and shock wave intensities much in excess of individual bubbles[24]. It is possible that this phenomenon could be used to advantage in sonochemistry.

Theoretical bubble dynamics. The field of cavitation bubble dynamics has been active for many years and has reached a considerable level of maturity (measured, but if by no other manner, by the complexity of the analytical development and the number of papers published on the subject annually.) However mature the field, the direct transfer of this knowledge to sonochemistry is not a simple matter. It would seem that increased interaction between those who are interested in sonochemistry for its yields and reaction rates (sonochemists?) with those more interested in the physical mechanisms that result in sonochemistry (sonophysicists?) would be of considerable benefit to both communities. It is clear that there is still a wide gulf between the two camps and meetings such as those held by the European Society of Sonochemistry (ESS) are of considerable benefit in enhancing communication between sonochemists and sonophysicists.

Pulsed enhancement. Because most sonochemists are concerned about reaction yields, it would seem of little benefit to pulse the acoustic field. However, because cavitation bubble dynamics is such a complex phenomenon, there are very likely certain situations in which sonochemistry could be enhanced by operating the acoustic source under pulsed conditions. As demonstrated in the studies of Flynn and Church[25] and Henglein and Gutierrez[26], certain effects are enhanced under pulsed conditions. A brief explanation for the phenomenon is as follows: a cavitation bubble grows from a nucleation site, and while expanded, gathers extra gas that diffuses into the bubble from the liquid. When the bubble collapses, it shatters into many smaller bubbles, which in turn can act as extra nucleation sites. However, there

is an optimal size for gas bubbles to act as nucleation sites. If the collapse produces bubbles that are too large and thus unfavourable for bubble growth, a delay in the time between pulses can be of benefit. Of course, a delay that is too long will result in the dissolution of these potential cavitation nuclei, which is clearly undesirable. Thus, certain pulse lengths and repetition frequencies can lead to an optimization of the effect. Because total energy consumption is a major factor in the industrial application of sonochemistry, there appears to be considerable promise for research efforts in this area.

Start-up time. If one observes the SL produced by a cavitation field, then turns off the field, and then again re-establishes the field, there is a readily observable 'start-up time', of the order of seconds before the SL is again observed. Since transient cavitation can occur within an acoustic cycle, it is difficult to explain the reason for this time delay. Apparently there are some steady-state conditions that need to be established. Because the characteristic time-scales for diffusion are of this order, it appears likely that this effect plays an important role. This delay time appears to have no positive consequences for sonochemistry, but its understanding may be of benefit to the global understanding of the general phenomenon.

Recommendations

It is presumptuous of the author, who is at best a novice in the field of sonochemistry, to offer recommendations; however, as an aspiring sonophysicist, and one accustomed to offering opinions on any topic, he boldly proceeds:

1 'Know thy sound field'. One of Apfel's golden rules[27] of cavitation is directly applicable here. Sonochemistry will not mature or gain acceptability as a science until discoveries in one laboratory can be duplicated in another laboratory (or industrial reactor). Since the sound field is the source of sonochemistry, it is recommended that accurate measurements be made and careful descriptions be presented of the characteristics of the field. Of course, in many cases, these measurements are either very difficult or nearly impossible. Hence, reactor designs that permit this determination are clearly desirable.

2 'Know thy liquid'. The second of Apfel's golden rules applies less directly but is still of considerable importance. Cavitation bubble dynamics is very dependent on such variables as the dissolved gas concentration (and composition) and liquid vapour pressure. It is less dependent on such parameters as viscosity, electrical conductivity, density and velocity of sound. Again, one could obtain radically different results for different values of some of these parameters. In a similar sense to the preceding section, it is recommended that those liquid properties be measured and presented whenever possible.

3 'Know thy dirt'. It is more appealing for sonophysicists to attempt first an understanding of homogeneous sonochemistry because of the complexity of the heterogeneous systems. However, as Apfel suggests in a corollary of his golden rule, the source of cavitation nucleation is most likely to originate on inhomogeneities that exist within the liquid. Further, heterogeneous sonochemistry would seem to have greater promise for industrial applications. Hence it is recommended

that efforts be made to understand the nucleation process as fundamental to the phenomenon of cavitation, and therein sonochemistry.

4 'Establish some benchmarks'. Before sonophysicists can make progress in understanding why sonochemistry works, they must be able to work with a few simple reactions that are easily performed and provide repeatable results. Therefore, it is recommended that a future committee of the ESS or some other interested organization provide a description of a few simple reactions with expected yields under carefully and thoroughly specified conditions of the sound field and the liquid. At least one reaction should involve heterogeneous sonochemistry.

5 'Establish an International Society'. At this nascent period in the development of the science of sonochemistry, there is considerable benefit associated with a professional community that provides opportunities for the diffusion of knowledge through meetings and written communications; further, it can lead to the establishment of standards, foster collaboration among scientists and between scientists and engineers, and generally promote the general welfare. Additionally, there is a critical mass in terms of the number of individuals before such Societies, with their inevitable ups and downs, cannot only endure but prevail. The ESS is currently on the road to success in reaching this critical mass and should now be ready to serve as the nucleus of an international society. Accordingly, it is recommended that the ESS combine with representatives of other budding national and regional societies to form the International Society of Sonochemistry.

Acknowledgements

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